

# STATISTICAL MECHANICS AND THERMODYNAMICS OF LIQUIDS AND LIQUID MIXTURES

Thesis submitted to the Faculty of Science  
for the Degree of

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in  
Science

by

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DEDICATION



*Dedicated to the loving memories of  
my mother*

**Late (Smt.) I. V. Singh.**

*She has been an inspiring force throughout  
my life.....*

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**CERTIFICATE**

This is to certify that **Mr. Vinod Kumar Singh** has fulfilled all the requirements for the submission of D. Phil. thesis entitled "**Statistical Mechanics and Thermodynamics of Liquids and Liquid Mixtures**" to the University of Allahabad. This is a record of the candidate's own effort under my guidance and supervision.

Allahabad

June 26, 2003

A handwritten signature in dark ink, appearing to read "J. D. Pandey".

(J. D. Pandey)

Supervisor

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(Vinod Kumar Singh)

## PREFACE

Molecular interactions are the key for understanding the structure and properties of liquids. The physico-chemical behaviour and nature of intermolecular interactions in the liquid mixtures have been a subject of active interest, and fascinating progress in the study of intermolecular forces has been made in the last few years. Despite the large number of measurements on binary liquid mixtures, very limited studies have included pressure as an experimental variable, and in only very few cases these studies have been done at pressures other than atmospheric.

Recently, study of the high pressure physics of liquids has become one of the most important fields in physical chemistry and chemical physics. But, due to scarcity of experimental data at elevated pressures, such studies could not be carried out for binary liquid mixtures. For the first time Takagi et al [J Chem Therm, **12**, 277 (1980); **14**, 1167 (1982); **16**, 1031 (1984); **17**, 1057 (1985); **20**, 809 (1988)] carried out accurate experimental measurements of ultrasonic velocity and related thermodynamic properties of some binary liquid mixtures at elevated pressures. In the present work, well-established Flory's statistical theory [Flory et al, J Am Chem Soc, **86**, 3507, 3515, 3563 (1964); **87**, 1833, 1838 (1965) & J D Pandey et al, J Chem Soc Faraday Trans I, **84**, 1853 (1988); J Am Chem Soc, **104**, 3299 (1982); J Chem Research (s), 344 (2001); J Mol Liq, **100/2**, 153 (2002)] has been modified and developed for high pressure. This pressure-dependent Flory theory has been used for the computation of various thermodynamic properties of pure liquids and binary liquid mixtures at elevated pressures.

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## **Chapter-1**

**Introduction and literature survey**

In the liquid state, thermodynamics and statistical mechanics can be used as a tool to further our knowledge about the interactions in liquid mixtures. Thermodynamics constitutes a very subtle study in physics, chemistry and engineering, and has innumerable applications. Statistical mechanics combines the laws of statistics with the laws of mechanics applicable to atomic or molecular particles. Thermodynamics presents broad relationship among the macroscopic properties but it is not concerned with the quantitative prediction of these properties. On the other hand, statistical mechanics seeks to establish relationship between macroscopic properties and intermolecular forces through partition functions and is very much concerned with the quantitative prediction of bulk properties. The statistical methods do not give the information of actual behaviour of the system but that of the maximum probability. The connection between statistical mechanics and thermodynamics is provided by entropy.

There are two main reasons for the large amount of experimental and theoretical work on the properties of liquid mixtures<sup>(1-6,43-47)</sup>. The first is that they provide one way of studying the physical forces acting between two molecules of different species. The second reason is the appearance of new phenomenon which are not present in pure substances.

Molecular interactions are the key for understanding the structure and properties of liquids. Nature of intermolecular interactions and thermodynamic behaviour of liquid mixtures have considerable significance in thermodynamics. Intermolecular forces on the whole are a very wide subject in the study of liquid mixtures. Various detailed theories and discussions in this regard have been given by Hirschfelder<sup>(1)</sup>, Margenau<sup>(2)</sup>, and Kihara<sup>(3)</sup> Rowlinson<sup>(4)</sup>, Hildebrand and co-workers<sup>(5)</sup> and Moelwyn-Hughes<sup>(6)</sup>.

The subject of intermolecular forces is important from the view-point of its applications in many branches of science. Many attempts have been made to understand intermolecular attractions since the designation of "regular-solution theory" by Hildebrand<sup>(7)</sup>. Prigogine and co-workers<sup>(8-11)</sup>

developed the cell model, and also gave a theory based on the explicit combination of the cell method and the "corresponding state theorem". Another statistical mechanical theory which has gained prominence is the "significant structure theory" developed by Eyring and his group<sup>(12-16)</sup>. This is a purely thermodynamic theory, and yielded excellent results for most of the properties in the case of pure liquids and liquid mixtures. But this theory is very cumbersome and required a number of molecular parameters for its application. The hard sphere models proposed by various workers<sup>(17-23)</sup> have also been used, in recent past, to estimate various thermodynamic properties of pure liquids and few binary liquid mixtures. Flory et al<sup>(24-27)</sup> used a simple partition function proposed by Eyring and Hirschfelder to get reduced equation of state which is based on the van der Waals potential energy model.

Out of various statistical mechanical theories used in past, Flory's statistical theory<sup>(24-27)</sup> has gained much popularity due to its simplicity and validity. It has been applied to pure liquids, binary and multicomponent liquid systems of molecular liquids, metallic liquids, alloys and ionic liquids. In most cases, this theory has been found to be superior. The simplicity and precision in prediction of various thermodynamic properties makes the Flory theory a subject of special interest. Coefficient of thermal expansion ( $\alpha$ ) and isothermal compressibility ( $\beta_T$ ) are the only two parameters of pure components which are needed for the computation of many thermodynamic properties. Moreover, it has no adjustable parameter. During recent years<sup>(28-41,102-105)</sup>, this theory has been widely used for estimating a number of properties of a variety of liquid mixtures.

Despite the large number of measurements on binary liquid mixtures, few studies have included pressure as an experimental variable, and in only very few cases these studies have been done at pressures other than the atmospheric. It is widely known that the pressure has a great influence on packing and other effects in the mixture, so such measurements are suitable for testing the various theories of the liquid state. In the past few years, the study of the high pressure physics of

liquids have become one of the most important fields in physical chemistry and chemical physics.

Excess thermodynamic properties provide information about the molecular interactions and macroscopic behaviour of liquid mixtures. Excess thermodynamic functions are sensitively dependent not only on the differences in molecular forces but also on the difference in the size and shape of molecules. Use of excess function results from the fact that statistical mechanical theories of liquid mixtures naturally lead to the prediction of theoretical values of excess functions.

There has been considerable interest<sup>(24-27,29,33)</sup> in the theoretical and experimental investigation of the excess thermodynamic properties of liquid mixtures during the last few years. From the theoretical point of view, excess properties at elevated pressures are of particular interest, as they allow to test the applicability of molecular theories to predict the thermodynamic behaviour of liquids and their mixtures at ambient conditions.

The study of excess compressibilities and excess volume provides important information on the intermolecular forces determining the properties of liquid mixtures. Excess molar volume reflects not only interactions but also difference between free volumes of the components. It has been established that the sign and magnitude of  $V^E$  give a good estimate of the strength of the unlike interactions in a binary mixture<sup>(42)</sup>.

Ultrasonic velocity has been found to be the most powerful tool for the structural and interaction studies of liquids and liquid mixtures. Ultrasonic propagation parameters and thermodynamic parameters are very important in understanding the physico-chemical behaviour of the liquid state. Measurement of sound velocity provides a convenient method for determining those properties of liquids which are not easily accessible by direct experimentation.

Measurements of ultrasonic velocity have been adequately employed in understanding the molecular interactions in pure liquids and liquid mixtures. The propagation of ultrasonic (sound) wave through a



medium is essentially a thermodynamic property, and is related to the physico-chemical properties of the system. Recent developments have made it possible to use ultrasonic waves in medicine, engineering, agriculture and chemical industry. Ultrasonic studies find extensive applications in almost every field of science.

Most of the physical, thermodynamic and acoustic properties of the liquid mixtures have been theoretically<sup>(47,48)</sup> derived from those of the components, by assuming that the dissimilar molecules are non-interacting. This case exists in mixtures where both the components are non-polar. In the binary mixture, where one component is polar and other is non-polar, interactions have been observed<sup>(49)</sup>. Even if the interaction between polar and non-polar molecules is weak, there will be considerable change in the molecular environment. In such a case, the physical, thermodynamic and acoustic properties are likely to be affected by intermolecular hydrogen bonding, dipole-dipole, dipole-induced dipole and charge transfer interaction between the unlike molecules due to the variation in the relative concentration of the components<sup>(49,50)</sup>.

Successful attempts have been made in the recent past<sup>(51-56)</sup> on theoretical evaluation of ultrasonic velocity and its correlation with other thermodynamic properties in binary liquid mixtures using statistical and semi-empirical theories.

Sound velocity depends on the density of the medium. The density of liquid mixture and related volumetric properties are required for many applicative aspects, as well as for theoretical calculations. Particularly, their knowledge is indispensable when the classical and thermodynamic approach is to be used to relate and to compute the equilibrium properties of mixtures. From this point of view, they are of strategically importance for both the test of existing theories and the development of new models for mixture behaviour.

Thermal expansion coefficient is a very important thermodynamic property and knowledge of this property helps in calculating various thermodynamic parameters. Recently<sup>(57)</sup> an empirical relation has been

proposed for computation of thermal expansivity which uses only the values of ultrasonic velocity and density at given temperature.

Isentropic compressibility is a highly useful property in understanding the nature of molecular interactions in liquid mixtures because it depends upon the volume, and volume is very sensitive to the intermolecular interactions in liquid mixtures. In recent years, there has been an increased interest in the determination of either isentropic compressibility or isothermal compressibility. The role that isentropic compressibility plays in the thermodynamic characterization of binary liquid mixtures is also a subject study in recent years<sup>(58)</sup>. The isentropic compressibility may be used to separate the contribution of pressure and temperature in the change of thermodynamic properties.

The more fundamental thermodynamic quantity is the isothermal rather than the isentropic compressibility and is fairly sensitive to a change of pressure. It is the key parameter in molecular thermodynamics of fluid phase equilibria.

Isothermal compressibility has been widely evaluated by many workers<sup>(19-21)</sup> for pure liquids but very limited attempts<sup>(17,59-61)</sup> have been made to evaluate isothermal compressibility for liquid mixtures.

One of the most important properties of the liquid state is the internal pressure which is the resultant of the forces of attraction and repulsion between the molecules of a liquid. The internal pressure of liquids is highly useful in understanding molecular interactions, internal structure, clustering phenomenon and ordered structure. Attempts have been made by Barton<sup>(62)</sup>, Rosseinsky<sup>(63)</sup>, Berkowitz et al<sup>(64)</sup>, Hildebrand et al<sup>(65)</sup> and Suryanarayana<sup>(66)</sup> to demonstrate the significance of internal pressure as a fundamental property of the liquid state and its correlation with other thermodynamic properties. Theoretical deduction of internal pressure of binary liquid mixtures was carried out by Subrahmanyam et al<sup>(67-69)</sup> using Flory's statistical theory.

Another quantity of interest is the Grüneisen parameter, which was originally defined for solids but has recently been shown to be useful in

studying liquids. The concept of Grüneisen parameter has been extended to liquid state for investigating the internal structure, clustering phenomenon and the remaining quasi-crystalline lattice nature. The Grüneisen parameter is a dimensionless measure of change in entropy with volume or thermal pressure. Several workers have evaluated internal pressure<sup>(67-71)</sup> and Grüneisen parameter<sup>(72,73)</sup> in binary liquid mixtures. But, as far as our knowledge is concerned, no work has, so far, been done on the pressure dependent properties of binary mixtures on the basis of Flory theory.

Heat capacity measurements<sup>(74,75)</sup> have been found to be useful in the investigation of change of liquid structure taking place during mixing. Heat capacity is unique amongst thermodynamic quantities as an indicator to changes of structure (i.e. order) or non-randomness in pure liquids and mixtures during the mixing process. The order-destruction and order-creation processes in mixtures can also be studied through determination of the corresponding excess quantity. Heat capacity measurements were carried out by Patterson et al<sup>(76,77)</sup> and Ahluwalia et al<sup>(78,79)</sup> during recent years. Flory's statistical theory has been utilized to estimate heat capacities in various binary mixtures but in only very few cases these estimation have been done at pressures other than atmospheric.

It is well known that the finite-amplitude waves travelling through a fluid will give rise to a number of non-linear phenomenon such as wave distortion, harmonic generation and sound saturation. It has become of much interest to predict the extent of various kinds of non-linear effects, which are due to deviation from linearity in ordinary acoustics<sup>(80-84)</sup>. The acoustician who studies finite-amplitude sound propagation in liquids is naturally interested in the non-linearity parameter,  $B/A$ , of liquids. The non-linearity parameter is a basic parameter for determining the degree of waveform distortion. It plays a significant role in non-linear acoustics and its determination is of increasing interest in a number of areas ranging from underwater acoustics to medical science. From the knowledge of the parameter of non-linearity, one can gain information about some physical

properties<sup>(85,86)</sup> of the liquids such as internal pressure, intermolecular spacing, acoustic scattering and structural behaviour etc.

Study of non-linearity parameter of liquid mixture is important in view of the information it may yield on the interaction in liquid mixtures. B/A values of the liquids have been interpreted as the quantity representing the magnitude of the hardness of liquid<sup>(87)</sup> which may be considered to be true for the liquid mixtures as well.

Beyer et al<sup>(80-82)</sup> were the first who presented the theoretical formalism of non-linearity parameter and determined it for a number of organic liquids using sound velocity and other thermodynamic data. During recent years<sup>(88-92,96-100)</sup>, a number of experimental and theoretical studies have been performed on the non-linearity parameter of liquids and liquid mixtures. Also, measurement of this parameter for biological media<sup>(93-95)</sup> including living tissues is one of the more recent interests as it can provide important information for the ultrasonic application in biological research related to diagnosis and therapy. Although detailed studies of the non-linearity parameter of liquids and liquid mixtures have been reported, to the best of our knowledge, computation of B/A at elevated pressures has not been done so far.

Thermophysical and thermoacoustical parameters have been successfully used to study the intermolecular interactions in liquids. These properties have been expressed in terms of the volume expansion, which is found as the controlling factor for their dependence on temperature and volume for liquids. Beyer's non-linearity parameter  $(B/A)^{(81,82)}$ , Rao's acoustical parameter  $(K)^{(101)}$  and the Grüneisen parameter  $(\Gamma)^{(72,73)}$  are all simply related to each other. All the thermoacoustical properties are obtained with the help of thermal expansion coefficient whose dependence on temperature and pressure may conveniently be utilized to obtain them.

Thus, it is evident that the study of the properties of liquid state consists of a wide range of problems and to discuss all of them will certainly not be exhaustive but practically beyond the scope of the present thesis. During the past few years, the study of the high pressure physics of

liquids has become one of the most important fields in physical chemistry and chemical physics. In the present thesis, some important thermophysical and thermoacoustical parameters of pure liquids and liquid mixtures have been evaluated using Flory's statistical theory at elevated pressures. As far as our knowledge is concerned, no work has, so far, been done on the pressure dependent properties of binary liquid mixtures on the basis of Flory theory. This is our first attempt to apply Flory theory for evaluating properties of binary liquid mixtures at elevated pressures.

The present investigative work entitled **"Statistical Mechanics and Thermodynamics of Liquids and Liquid Mixtures"** is compiled in forthcoming eight chapters. The entire thesis work encompasses theoretical predictions and interpretations of thermodynamic and other properties of liquid mixtures.

Chapter-1 of the present thesis is introductory. It is devoted for the objective, scope and outline of the present work. An upto-date literature survey alongwith the background of the work is presented in this chapter. At the end of this chapter brief outline of the work presented in the subsequent chapters are given.

Recently, extensive work on Flory theory has been done in substantial amount at atmospheric pressure. In chapter-2 of the thesis, Flory theory has been developed for high pressure to evaluate various thermodynamic properties of liquids and liquid mixtures.

In chapter-3 of this thesis, the values of excess volume, density and thermal expansion coefficient of two binary liquid mixtures e. g. toluene + o-xylene and toluene + aniline, have been computed at elevated pressures and at temperature of 303.15 K using Flory's statistical theory by the method described in the previous chapter.

The aim of chapter-4 is to evaluate internal pressure and pseudo-Grüneisen parameter of two binary liquid mixtures using pressure-dependent Flory's statistical theory at temperature 303.15 K. The binary mixtures under consideration are toluene + o-xylene and toluene + aniline.

Chapter-5 of the thesis deals with the computation of heat capacity at constant pressure, heat capacity at constant volume and heat capacities ratio of the above mentioned binary liquid mixtures using Flory theory at temperature 303.15 K and at pressures ranging from 0.1 MPa to 160 MPa. Excess heat capacities of the liquid mixtures have also been reported.

Chapter-6 comprises the theoretical predictions of ultrasonic velocity, isothermal and isentropic compressibilities of the two binary mixtures viz. toluene + o-xylene and toluene + aniline at elevated pressures and at temperature 303.15 K for four different mole fractions using Flory theory.

Chapter-7 deals with the computation of acoustic non-linearity parameter,  $B/A$ , of pure liquids e.g. toluene, o-xylene and aniline at elevated pressures and at temperature of 303.15 K using different approaches. The different methods used are Ballou's empirical relation, Hartmann's relation, Tong-Dong method using Schaaffs equation for sound velocity and Sharma's method. A comparative study of  $B/A$  values obtained from different methods has also been carried out.

Chapter-8 consists of the theoretical evaluation of non-linearity parameter of binary liquid mixtures. The mixture under present investigation are toluene + o-xylene and toluene + aniline. The methods used and the conditions are the same as employed in the previous chapter.

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## **Chapter-2**

Theoretical formalism of thermodynamic properties  
of liquid mixtures on the basis of Flory's statistical  
theory - pressure dependent studies

## Introduction :

There has been an increasing interest in the study of thermodynamic functions as they are useful in understanding the nature of intermolecular interactions between component molecules of a mixture. Among all the theories, known so far, the Flory's statistical theory<sup>(1-6)</sup> has been the most widely applied theory of liquid mixtures. It has been employed to describe the thermodynamic behavior of binary and multicomponent systems by various workers<sup>(7-18)</sup>. But, it appears from literature survey that most of the studies have been limited to zero pressure<sup>(7-18)</sup>, and no attempt has been made, so far, to evaluate the thermodynamic properties of pure and binary liquid mixtures at elevated pressures.

For the first time Takagi et al<sup>(20-24)</sup> carried out experimental measurements of ultrasonic velocity and related thermodynamic properties of some binary liquid mixtures at elevated pressures.

The present work deals with the theoretical evaluation of various thermodynamic properties of pure liquids and binary liquid mixtures at elevated pressures. Here the reduced equation of state<sup>(4)</sup> due to Flory is solved to get expressions for the thermal expansion coefficient ( $\alpha$ ) and isothermal compressibility ( $\beta_T$ ) under the restriction of pressure considerations. Further, pressure - dependent expressions are derived for the reduced volume ( $\tilde{V}$ ) and reduced pressure ( $\tilde{P}$ ) which are used to get the different thermodynamic properties of pure components and binary mixtures namely, toluene + o-xylene and toluene + aniline.

## Theory :

According to Flory's statistical theory<sup>(4)</sup>, based on van der Waals potential energy model, the reduced equation of state is given by

$$\frac{\tilde{P} \tilde{V}}{\tilde{T}} = \frac{\tilde{V}^{1/3}}{\tilde{V}^{1/3} - 1} - \frac{1}{\tilde{V} \tilde{T}} \quad \text{-----}(2.1)$$

where the reduced parameters  $\tilde{V}$ ,  $\tilde{T}$  and  $\tilde{P}$  are given by

$$\begin{aligned}\tilde{V} &= V/V^* \\ \tilde{T} &= T/T^*\end{aligned}\quad \text{----- (2.2)}$$

and,  $\tilde{P} = P/P^*$

Rearranging eq. (2.1), we get,

$$\tilde{T} = \frac{(\tilde{V}^{1/3} - 1)(\tilde{P}\tilde{V}^2 + 1)}{\tilde{V}^{4/3}} \quad \text{----- (2.3)}$$

or,

$$\tilde{T} = \tilde{P}\tilde{V} + \tilde{V}^{-1} - \tilde{P}\tilde{V}^{2/3} - \tilde{V}^{-4/3} \quad \text{----- (2.4)}$$

Differentiating eq.(2.4) with respect to  $\tilde{T}$  keeping  $\tilde{P}$  constant, we have

$$1 = \left[ \tilde{P} - \tilde{V}^{-2} - \frac{2}{3} \tilde{P} \tilde{V}^{-1/3} + \frac{4}{3} \tilde{V}^{-7/3} \right] \left( \frac{\partial \tilde{V}}{\partial \tilde{T}} \right)_{\tilde{P}}$$

$$\text{or,} \quad \left( \frac{\partial \tilde{V}}{\partial \tilde{T}} \right)_{\tilde{P}} = \frac{1}{\left[ \tilde{P} - \tilde{V}^{-2} - \frac{2}{3} \tilde{P} \tilde{V}^{-1/3} + \frac{4}{3} \tilde{V}^{-7/3} \right]} \quad \text{----- (2.5)}$$

Again, differentiating eq. (2.4) with respect to  $\tilde{P}$  keeping  $\tilde{T}$  constant and rearranging, we obtain,

$$\left( \frac{\partial \tilde{V}}{\partial \tilde{P}} \right)_{\tilde{T}} \left[ \tilde{V}^{-2} + \frac{2}{3} \tilde{P} \tilde{V}^{-1/3} - \frac{4}{3} \tilde{V}^{-7/3} - \tilde{P} \right] = \tilde{V}^{2/3} (\tilde{V}^{1/3} - 1) \quad \text{---- (2.6)}$$

The coefficient of thermal expansion ( $\alpha$ ) and isothermal compressibility ( $\beta_T$ ) may be expressed in terms of reduced variables as<sup>(1)</sup>,

$$\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P = \frac{\tilde{T}}{T \tilde{V}} \left( \frac{\partial \tilde{V}}{\partial \tilde{T}} \right)_{\tilde{P}} \quad \text{----- (2.7)}$$

and ,

$$\beta_T = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T = -\left( \frac{\tilde{P}}{P \tilde{V}} \right) \left( \frac{\partial \tilde{V}}{\partial \tilde{P}} \right)_{\tilde{T}} \quad \text{----- (2.8)}$$

Now using eqs. (2.5) and (2.6) in eqs. (2.7) and (2.8) respectively, and solving to eliminate  $\tilde{T}$  in each case, we get

$$(\alpha T)^{-1} = \frac{2\tilde{P}\tilde{V}^2}{(\tilde{P}\tilde{V}^2 + 1)} + \frac{1}{3(\tilde{V}^{1/3} - 1)} - 1 \quad \text{----- (2.9)}$$

and

$$(\beta_T P)^{-1} = \left\{ 1 + \frac{1}{\tilde{P}\tilde{V}^2} \right\} \left\{ \frac{1}{3(\tilde{V}^{1/3} - 1)} - 1 \right\} + 2 \quad \text{----- (2.10)}$$

Solving eqs. (2.9) and (2.10) together, and rearranging we obtain

$$\tilde{V} = \left[ 1 + \frac{\alpha T}{3(1 - 2\beta_T P + \alpha T)} \right]^3 \quad \text{----- (2.11)}$$

Using this value of  $\tilde{V}$  is eq. (2.9), we get

$$\tilde{P} = \frac{\beta_T P}{(\alpha T - \beta_T P)} \left[ \frac{1}{1 + \frac{\alpha T}{3(1 - 2\beta_T P + \alpha T)}} \right]^6 \quad \text{----- (2.12)}$$

Thus, with the knowledge of thermal expansion coefficient and isothermal compressibility, we can calculate reduced volume ( $\tilde{V}$ ) and reduced pressure ( $\tilde{P}$ ) for pure components at elevated pressures with the help of eqs. (2.11) and (2.12). Equations (2.11) and (2.12) are the pressure-dependent expressions for the reduced volume and reduced pressure. Reduced temperature ( $\tilde{T}$ ) can be calculated from eq. (2.3) using the values of  $\tilde{V}$  and  $\tilde{P}$ . Characteristic parameters can be obtained with the help of eq. (2.2).

### Binary Liquid Mixtures :

Segment fraction ( $\psi$ ) and site fraction ( $\theta$ ) of liquid mixtures have been computed by the method suggested earlier<sup>(8,9,11,18)</sup> according to which

$$\psi_i = \frac{x_i V_i^*}{\sum x_i V_i^*} \quad \text{----- (2.13)}$$

where  $V_i^*$  is the characteristic volume of the  $i^{\text{th}}$  pure component and

$$\theta_i = \frac{\psi_i}{\psi_i + \sum_{k \neq i} \psi_k \left( \frac{V_i^*}{V_k^*} \right)^{1/3}} \quad \text{-----(2.14)}$$

thus for binary mixtures, the segment fractions and site fractions will be

$$\psi_2 = \frac{x_2 V_2^*}{x_1 V_1^* + x_2 V_2^*} \text{ and } \psi_1 = 1 - \psi_2 \quad \text{-----(2.15)}$$

and,

$$\theta_2 = \frac{\psi_2}{\psi_2 + \psi_1 \left( \frac{V_2^*}{V_1^*} \right)^{1/3}} \text{ and } \theta_1 = 1 - \theta_2 \quad \text{-----(2.16)}$$

The interaction parameter  $X_{ij}$  is defined as<sup>(8,9,11,18)</sup>

$$X_{ij} = P_i^* \left[ 1 - \left( \frac{P_j^*}{P_i^*} \right)^{1/2} \left( \frac{V_j^*}{V_i^*} \right)^{1/6} \right]^2 \quad \text{-----(2.17)}$$

where  $P_i^*$  and  $P_j^*$  are characteristic pressures of pure components  $i$  and  $j$ .

For binary liquid mixtures, there is only one Flory's interaction parameter term  $X_{12}$  which is expressed as,

$$X_{12} = P_1^* \left[ 1 - \left( \frac{P_2^*}{P_1^*} \right)^{1/2} \left( \frac{V_2^*}{V_1^*} \right)^{1/6} \right]^2 \quad \text{-----(2.18)}$$

The characteristic pressure  $P^*$  for the mixture is calculated by the following equations<sup>(8,9,11,18)</sup>



$$P^* = \left[ \left( \sum_i \psi_i P_i^* \right) - \left( \sum_{j \neq i} \psi_i \theta_j X_{ij} \right) \right] \quad \text{----(2.19)}$$

thus, for binary mixtures

$$P^* = \left[ (\psi_1 P_1^* + \psi_2 P_2^*) - (\psi_1 \theta_2 X_{12}) \right] \quad \text{----(2.20)}$$

The characteristic temperature  $T^*$  of the mixture is given by<sup>(8,9,11,18)</sup>

$$T^* = \frac{P^*}{\left[ \sum_i \left( \frac{\psi_i P_i^*}{T_i^*} \right) \right]} \quad \text{----(2.21)}$$

For binary mixtures  $T^*$  will be

$$T^* = \frac{P^*}{\left[ \frac{\psi_1 P_1^*}{T_1^*} + \frac{\psi_2 P_2^*}{T_2^*} \right]} \quad \text{----(2.22)}$$

and the reduced temperature  $\tilde{T}$  of the mixture is given by

$$\tilde{T} = \frac{T}{T^*} \quad \text{---- (2.23)}$$

The ideal reduced volume  $\tilde{V}^0$  is given by

$$\tilde{V}^0 = \sum_i x_i \tilde{V}_i \quad \text{---- (2.24)}$$

For binary mixture

$$\tilde{V}^0 = x_1 \tilde{V}_1 + x_2 \tilde{V}_2 \quad \text{---- (2.25)}$$

The ideal reduced temperature  $\tilde{T}^0$  is defined with the help of eq. (2.3)

$$\tilde{T}^0 = \frac{\left( \tilde{V}^0^{1/3} - 1 \right) \left( \tilde{P}^0 \tilde{V}^0 + 1 \right)}{\tilde{V}^0^{4/3}} \quad \text{----(2.26)}$$

The excess reduced volume,  $\tilde{V}^E$ , is defined as<sup>(2,5)</sup>

$$\tilde{V}^E = \left( \frac{\partial \tilde{V}}{\partial \tilde{T}} \right)_{\tilde{P}} (\tilde{T} - \tilde{T}^0)$$

using eq. (2.5), with negligible approximation, we get

$$\tilde{V}^E = \left[ \tilde{P} - \tilde{V}^{0.2} - \frac{2}{3} \tilde{P} \tilde{V}^{0.4} + \frac{4}{3} \tilde{V}^{0.6} \right]^{-1} (\tilde{T} - \tilde{T}^0) \quad \text{-----(2.27)}$$

The reduced volume,  $\tilde{V}$ , for the mixture is given by

$$\tilde{V} = \tilde{V}^0 + \tilde{V}^E \quad \text{-----(2.28)}$$

with this value of reduced volume  $\tilde{V}$  of the mixture, various parameters for the liquid mixture can be calculated.

### Excess Volume ( $V^E$ ) :

The excess volume of the mixture is calculated with the help of equation<sup>(10)</sup>.

$$V^E = \left( \sum x_i V_i^* \right) \tilde{V}^E \quad \text{---- (2.29)}$$

### Thermal Expansion Coefficient ( $\alpha$ ) :

Thermal expansion coefficient of the mixture is calculated with the help of pressure – dependent expression given by

$$\alpha = \frac{1}{T} \left[ \frac{2\tilde{P}\tilde{V}^2}{(\tilde{P}\tilde{V}^2 + 1)} + \frac{1}{3(\tilde{V}^{1/3} - 1)} - 1 \right]^{-1} \quad \text{---- (2.30)}$$

### Isothermal Compressibility ( $\beta_T$ ):

The pressure–dependent expression for the isothermal compressibility is given as

$$\beta_T = \frac{1}{P} \left[ \left\{ 1 + \frac{1}{\tilde{P}\tilde{V}^2} \right\} \left\{ \frac{1}{3(\tilde{V}^{1/3} - 1)} - 1 \right\} + 2 \right]^{-1} \quad \text{---- (2.31)}$$

### Internal Pressure ( $P_i$ ) :

Internal pressure is related to the thermal expansion coefficient and isothermal compressibility through the relation,

$$P_i = \frac{\alpha T}{\beta_T} - P \quad \text{---- (2.32)}$$

### Heat Capacity at Constant Pressure ( $C_p$ ) :

Heat capacity at constant pressure of the mixture is defined as,

$$C_p = C_p(idl.) + C_p^E \quad \text{---- (2.33)}$$

where  $C_p(idl.)$  is the ideal heat capacity of the mixture and is defined as,

$$C_p(idl.) = \sum x_i C_{pi} \quad \text{---- (2.34)}$$

where  $C_{pi}$  is the heat capacity of  $i^{\text{th}}$  pure component

The excess heat capacity,  $C_p^E$ , is defined by Khanwalkar et al.<sup>(12)</sup> according to Flory theory as,

$$C_p^E = \frac{P^* V^*}{T^*} \left[ \frac{1}{\left( \frac{4}{3} \bar{V}^{-1/3} - 1 \right)} - \sum_i \left( \frac{X_i}{\frac{4}{3} \bar{V}_i^{-1/3} - 1} \right) \right] \quad \text{---- (2.35)}$$

For binary mixtures, eq.(2.35) reduces to

$$C_p^E = \frac{P^* V^*}{T^*} \left[ \frac{1}{\left( \frac{4}{3} \bar{V}^{-1/3} - 1 \right)} - \left\{ \frac{X_1}{\left( \frac{4}{3} \bar{V}_1^{-1/3} - 1 \right)} + \frac{X_2}{\left( \frac{4}{3} \bar{V}_2^{-1/3} - 1 \right)} \right\} \right] \quad \text{---- (2.36)}$$

### Adiabatic Compressibility ( $\beta_s$ ) :

From the well-known thermodynamic relation

$$\beta_T - \beta_s = \frac{\alpha^2 T V}{C_p} \quad \text{---- (2.37)}$$

we get,

$$\beta_s = \beta_T - \frac{\alpha^2 TV}{C_p} \quad \text{-----(2.38)}$$

with the help of this equation, we can calculate the value of adiabatic compressibility for the liquid mixtures knowing  $\alpha$ ,  $\beta_T$  and  $C_p$ .

### Heat Capacities Ratio ( $\gamma$ ) :

The well-known thermodynamic relation for the heat capacities ratio is given as,

$$\gamma = \frac{\beta_T}{\beta_s} \quad \text{---- (2.39)}$$

### Heat Capacity at Constant Volume ( $C_V$ ) :

The heat capacity at constant volume of the mixture is calculated by the relation

$$C_V = \frac{C_p}{\gamma} \quad \text{---- (2.40)}$$

### Pseudo – Grüneisen Parameter ( $\Gamma$ ) :

Pseudo-Grüneisen parameter of the mixture can be expressed as<sup>(19)</sup>

$$\Gamma = \frac{\gamma - 1}{\alpha T} \quad \text{---- (2.41)}$$

### Density ( $\rho$ ) :

The molar volume ( $V$ ) of the mixture is related with the characteristic volume ( $V^*$ ) and reduced volume ( $\tilde{V}$ ) of the mixture as,

$$V = V^* \tilde{V} \quad \text{---- (2.42)}$$

where

$$V^* = \sum x_i V_i^* \quad \text{---- (2.43)}$$

and  $\tilde{V}$  is obtained from eq. (2.28).

We know that density is defined as

$$\rho = \frac{M_m}{V} \quad \text{---- (2.44)}$$

where  $M_m$  is the molecular weight of the mixture given by

$$M_m = \sum x_i M_i \quad \text{---- (2.45)}$$

where  $M_i$  is the molecular weight of the  $i^{\text{th}}$  pure component.

Thus, with the help of eq. (2.44), we can calculate the theoretical values of density for the mixture.

#### Ultrasonic Velocity( $u$ ) :

Ultrasonic velocity of the mixture can be calculated with the help of equation ,

$$u = \left( \frac{1}{\beta_S \rho} \right)^{1/2} \quad \text{---- (2.46)}$$

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### **Chapter-3**

Computation of excess volume, density and thermal expansivity at higher pressures using Flory's statistical theory

## Introduction:

The deviations from ideal behaviour can best be expressed in terms of excess thermodynamic functions<sup>(1)</sup>, which give more quantitative idea about the nature of molecular interactions. The difference between the thermodynamic function of mixing for a real system and the corresponding value for an ideal system at the same temperature and pressure is called thermodynamic excess function. It is denoted by superscript E. This quantity represents the excess (positive or negative) of a given thermodynamic property of the solution over that in the ideal solution. e.g.

$$X^E = X - X_{\text{id}}$$

Excess thermodynamic properties<sup>(2)</sup> provide information about the molecular interactions and macroscopic behaviour of liquid mixtures, and can be used to test, and to improve thermodynamic models for calculating and predicting fluid phase equilibria. Excess thermodynamic functions are sensitively dependent not only on the difference in intermolecular forces but also on the difference in size and shape of molecules.

During the last few years<sup>(3)</sup>, the interest in experimental and theoretical work on thermodynamic properties of liquid mixtures at elevated pressures has greatly increased. From the theoretical point of view, excess properties at elevated pressures are of particular interest, as they allow to test the applicability of molecular theories to predict the thermodynamic behaviour of liquids and their mixtures at these conditions.

Values of excess molar volume provide a very sensitive test for the molecular solution theory. It has been observed that the  $V^E$  of mixing of two liquids can arise from any one or more of the following factors:

- (I) difference in size and shape of the component molecules,
- (II) structural changes, such as changes in the correlation of molecular orientation,



- (III) differences in the intermolecular interaction energy between like and unlike molecules, and
- (iv) formation of new chemical species through hydrogen bonding or electron donor acceptor interactions. Normally, volume changes occur because of the combination of these volume factors.

Excess molar volume,  $V^E$ , reflects not only interactions but also difference between free volumes of the components. The excess volume can be divided into two terms<sup>(5)</sup>;  $V_{size}^E$ , associated with the size difference of molecules and the other  $V_{int}^E$ , associated with the interaction forces between molecules. Thus, for a liquid mixture, we have

$$V^E = V_{size}^E + V_{int}^E$$

The term  $V_{size}^E$  is negative if the radii of both components are different, and is zero if the radii are equal. The values of  $V_{int}^E$  are observed to be negative or positive. This term is regarded as the excess volume which occurs from an interaction between molecules.

It has been established that the sign and magnitude of  $V^E$  give a good estimate of the strength of the unlike interactions in a binary mixture<sup>(6)</sup>. Large positive excess volume are taken as indicative of weak intermolecular interactions where as large negative values of excess volume are usually found when the interactions are strong and intermolecular complexes are believed to form. Extensive work on excess volume of liquid mixtures has already been carried out and still in progress by various workers<sup>(7-12)</sup>.

A number of thermodynamic properties can be evaluated when the sound velocity data are combined with density, pressure and temperature. Ultrasonic velocity, in conjunction with density measurements, permits the direct estimation of adiabatic compressibility ( $\beta_s$ ) and other related parameters which are not easily accessible by any other means.

Thermal expansion coefficient ( $\alpha$ ) is a very important thermodynamic property and knowledge of this property helps in calculating various thermodynamic parameters. Recently <sup>(13)</sup>, an empirical relation has been proposed for computation of thermal expansivity which uses only the values of ultrasonic velocity and density at given temperature.

In the present work, the values of excess volume, density and thermal expansion coefficient of binary liquid mixtures have been computed at elevated pressures using Flory's statistical theory by the method described in chapter two. For the prediction of thermal expansion coefficient of liquid mixtures, the reduced and characteristic parameters are calculated with the help of thermal expansion coefficient and isothermal compressibility of pure components. Molecular weights of the pure components are taken from the literature<sup>(4)</sup>. Here, we have used recently proposed relations<sup>(13,15)</sup> for computation of thermal expansion coefficient and isothermal compressibility of pure components,

$$\alpha = \frac{75.6 * 10^{-3}}{T^{1/9} u^{1/2} \rho^{1/3}} \quad \text{.....(3.1)}$$

$$\beta_T = \frac{17.1 * 10^{-4}}{T^{4/9} \rho^{4/3} u^2} \quad \text{.....(3.2)}$$

The other parameters of pure components are calculated as follows:

**Isentropic compressibility ( $\beta_S$ ):** Isentropic Compressibility have been calculated using the well-known thermodynamic relation,

$$\beta_S = \frac{1}{u^2 \rho} \quad \text{.....(3.3)}$$

where the experimental values of ultrasonic velocity and density of pure components are taken from the paper of Takagi et al<sup>(14)</sup>

**Heat Capacity at Constant Pressure ( $C_P$ ):** It is given as,

$$C_P = \frac{\alpha^2 TV}{\beta_T - \beta_S} \quad \dots(3.4)$$

**Heat Capacities Ratio ( $\gamma$ ):** The well-known thermodynamic relation for the heat capacities ratio is given as,

$$\gamma = \frac{\beta_T}{\beta_S} \quad \dots(3.5)$$

**Heat Capacity at Constant Volume ( $C_V$ ):** The heat capacity at constant volume is calculated by the relation,

$$C_V = \frac{C_P}{\gamma} \quad \dots(3.6)$$

**Pseudo- Grüneisen Parameter ( $\Gamma$ ):** Pseudo- Grüneisen parameter can be expressed as,

$$\Gamma = \frac{\gamma - 1}{\alpha T} \quad \dots(3.7)$$

**Internal Pressure ( $P_i$ ):** Internal pressure is related to the thermal expansion coefficient and isothermal compressibility through the relation,

$$P_i = \frac{\alpha T}{\beta_T} - P \quad \dots(3.8)$$

All these parameters of pure liquid components are reported in table 3.1.

**Theory:**

Equations (2.29), (2.30) and (2.44) have been used to obtain the values of excess volume, thermal expansion coefficient and density respectively of the binary liquid mixtures under consideration.

## Results and Discussion:

The values of excess volume, density and thermal expansivity of two binary mixtures have been evaluated with the help of Flory's statistical theory at elevated pressures, and at constant temperature of 303.15 K. The two binary liquid mixtures under the present consideration are: toluene + o-xylene and toluene + aniline.

The density and ultrasonic velocity of pure liquid components and binary mixtures are taken from the literature<sup>(14)</sup>. Thermal expansivity and isothermal compressibility of pure liquids are evaluated from relations (3.1) and (3.2). The desired characteristic and reduced parameters have been calculated using the methods discussed in chapter two. All the parameters of pure liquid components are taken from table 3.1. Tables 3.2 and 3.3 enlist the computed values of excess volumes of binary mixtures toluene + o-xylene and toluene + aniline respectively. Tables 3.4 and 3.5 enlist the experimental and computed values of density alongwith the percentage deviations at different compositions of toluene + o-xylene and toluene + aniline respectively. Tables 3.6 and 3.7 contain the experimental and computed values of thermal expansion coefficient alongwith the percentage deviations at different concentrations for the respective mixtures.

A close perusal of table 3.2 shows that the computed values of excess volume for toluene + o-xylene are, generally, positive in magnitude with very few exceptions at higher pressure side, indicating weak interactions between component liquids. But in the case of toluene + aniline (table 3.3) the values of excess volumes are found to be negative, which show strong interaction between component molecules of the mixture.

From tables 3.4 and 3.5, it is clear that computed values of density show the same trend as experimental one for both liquid mixtures under the present investigation. For both the liquid mixtures, the tables show that as the mole fraction of toluene in the mixture decreases, the density of the mixtures increases for the entire range of pressure. It is also

clear that for each mole fraction, the value of density increases as the pressure increases. The percentage deviations are found to be less than one for toluene + o-xylene, and for toluene + aniline it is found to be somewhat greater but maximum value is below ten percent. Tables 3.6 and 3.7 reveal that the computed values of thermal expansion coefficient for both the mixtures toluene + o-xylene and toluene + aniline show same trend as experimental one. For both the liquid mixtures, it is clear that as the mole fraction of toluene in the mixture decreases, thermal expansivity decreases over the entire range of pressure. Also, the values of thermal expansion coefficient decrease as the pressure increases at all mole fractions with a very few exceptions in the case of toluene + aniline. Percentage deviations are less than one for toluene + o-xylene and less than three percent with some exceptions for toluene + aniline system.

Table 3.1

Properties of pure components at 303.15 K

Toluene														
Pressure (MPa)	$\rho$ ( $\text{g cm}^{-3}$ )	$u$ ( $\text{m sec}^{-1}$ )	$\alpha \times 10^3$ ( $\text{K}^{-1}$ )	$\beta_1 \times 10^{12}$ ( $\text{cm}^2 \text{dyn}^{-1}$ )	$V$	$V^*$ ( $\text{cm}^3 \text{mol}^{-1}$ )	$T^*$ (K)	$P$	$P^* \times 10^7$ ( $\text{dyn cm}^{-2}$ )	$\beta_s \times 10^{12}$ ( $\text{cm}^2 \text{dyne}^{-1}$ )	$C_p$ ( $\text{J K}^{-1} \text{mol}^{-1}$ )	$\gamma$	$C_v$ ( $\text{J K}^{-1} \text{mol}^{-1}$ )	$\Gamma$ $\text{Pl} \times 10^{-7}$ ( $\text{dyn cm}^{-2}$ )
0.1	0.8580	1285.8	1.176	100.09	1.2865	83.4810	4840.31	0.00017	589.34	70.50	152.14	1.420	107.16	1.1775
10	0.8657	1334.3	1.151	91.84	1.2858	82.7837	4721.67	0.01635	611.54	64.88	158.54	1.416	112.00	1.1909
20	0.8729	1378.7	1.129	85.08	1.2851	82.1462	4615.28	0.03168	631.41	60.27	164.46	1.412	116.50	1.2026
30	0.8796	1421.6	1.109	79.21	1.2842	81.5773	4522.06	0.04611	650.59	56.26	170.20	1.408	120.88	1.2136
40	0.8858	1461.3	1.091	74.26	1.2834	81.0536	4437.05	0.05988	667.96	52.87	175.55	1.405	124.97	1.2233
50	0.8917	1499.9	1.075	69.87	1.2825	80.5779	4360.98	0.07301	684.83	49.85	180.78	1.402	128.98	1.2326
60	0.8972	1535.1	1.060	66.15	1.2817	80.1263	4288.80	0.08576	699.64	47.30	185.60	1.399	132.69	1.2405
70	0.9025	1567.0	1.047	63.00	1.2812	79.6989	4219.06	0.09826	712.38	45.13	190.01	1.396	136.11	1.2473
80	0.9075	1601.0	1.034	59.91	1.2802	79.3183	4159.36	0.11009	726.70	42.99	194.68	1.393	139.71	1.2549
90	0.9122	1630.3	1.023	57.37	1.2796	78.9402	4097.85	0.12196	737.92	41.24	198.78	1.391	142.90	1.2607
100	0.9168	1659.3	1.013	55.02	1.2790	78.5883	4041.01	0.13350	749.05	39.62	202.84	1.389	146.07	1.2664
110	0.9212	1688.0	1.002	52.83	1.2783	78.2597	3988.36	0.14472	760.08	38.10	206.87	1.387	149.20	1.2721
120	0.9253	1716.1	0.993	50.80	1.2775	77.9502	3938.95	0.15568	770.80	36.70	210.82	1.384	152.28	1.2776
130	0.9294	1742.0	0.984	49.02	1.2770	77.6476	3889.47	0.16666	780.03	35.46	214.50	1.382	155.16	1.2824
140	0.9333	1768.2	0.975	47.26	1.2762	77.3718	3845.91	0.17714	790.32	34.23	218.34	1.380	158.16	1.2877
150	0.9370	1794.0	0.967	45.71	1.2756	77.0984	3801.21	0.18775	798.95	33.16	221.89	1.379	160.95	1.2921
160	0.9407	1816.0	0.960	44.38	1.2752	76.8235	3754.22	0.19862	805.56	32.24	225.09	1.377	163.48	1.2956

## o-Xylene

Pressure (MPa)	$\rho$ ( $\text{gm cm}^{-3}$ )	$u$ ( $\text{m sec}^{-1}$ )	$\alpha \times 10^3$ ( $\text{K}^{-1}$ )	$\beta_L \times 10^{12}$ ( $\text{cm}^2 \text{dyn}^{-1}$ )	$V_L$	$V^*$ ( $\text{cm}^3 \text{mol}^{-1}$ )	$T^*$ (K)	$P_L$	$P^* \times 10^7$ ( $\text{dyn cm}^{-2}$ )	$\beta_S \times 10^{12}$ ( $\text{cm}^2 \text{dyne}^{-1}$ )	$C_p$ ( $\text{J K}^{-1} \text{mol}^{-1}$ )	$\gamma$	$C_v$ ( $\text{J K}^{-1} \text{mol}^{-1}$ )	$\Gamma$	$P_L \times 10^7$ ( $\text{dyn cm}^{-2}$ )
0.1	0.8714	1329.5	1.150	91.70	1.2815	95.0708	4893.98	0.00016	624.47	64.92	182.57	1.412	129.26	1.1825	537.08
10	0.8784	1377.4	1.127	84.52	1.2808	94.3691	4782.68	0.01546	646.77	60.00	189.87	1.409	134.79	1.1958	559.51
20	0.8850	1418.4	1.108	78.91	1.2803	93.6991	4678.64	0.03008	664.92	56.16	196.24	1.405	139.66	1.2061	578.11
30	0.8912	1459.8	1.090	73.81	1.2795	93.1043	4588.35	0.04389	683.56	52.65	202.66	1.402	144.57	1.2165	597.40
40	0.8971	1504.1	1.071	68.92	1.2782	92.5906	4513.58	0.05679	704.40	49.27	209.50	1.399	149.77	1.2281	619.04
50	0.9026	1539.8	1.057	65.23	1.2775	92.0727	4436.97	0.06947	719.78	46.73	215.14	1.386	154.11	1.2362	636.44
60	0.9079	1584.0	1.040	61.16	1.2759	91.6575	4381.16	0.08095	741.17	43.90	221.97	1.393	159.32	1.2477	657.94
70	0.9129	1607.3	1.030	58.97	1.2761	91.1429	4301.36	0.09353	748.40	42.40	225.87	1.391	162.42	1.2510	666.53
80	0.9176	1638.7	1.019	56.34	1.2754	90.7180	4238.74	0.10508	761.33	40.58	230.92	1.388	166.33	1.2575	680.86
90	0.9222	1667.7	1.008	54.04	1.2748	90.3087	4179.78	0.11648	772.70	38.99	235.62	1.386	170.00	1.2632	693.73
100	0.9266	1690.6	1.000	52.25	1.2747	89.8867	4114.50	0.12824	779.80	37.76	239.46	1.384	173.04	1.2666	702.47
110	0.9308	1721.8	0.989	50.07	1.2738	89.5467	4057.50	0.13872	792.97	36.24	244.47	1.382	176.94	1.2732	717.28
120	0.9349	1748.9	0.980	48.25	1.2731	89.2023	4017.64	0.14938	803.31	34.97	248.91	1.380	180.41	1.2783	729.36
130	0.9388	1773.2	0.972	46.68	1.2727	88.8603	3966.57	0.16016	811.68	33.68	252.95	1.378	183.59	1.2824	739.54
140	0.9426	1797.0	0.964	45.20	1.2722	88.5345	3917.89	0.17078	819.76	32.85	256.91	1.376	186.72	1.2864	749.50
150	0.9463	1820.4	0.957	43.82	1.2718	88.2239	3871.56	0.18124	827.61	31.89	260.82	1.374	189.80	1.2903	759.28
160	0.9498	1847.6	0.948	42.33	1.2709	87.9555	3835.05	0.19083	838.45	30.84	265.27	1.372	193.29	1.2956	772.06

## Aniline

Pressure (MPa)	$\rho$ (gm cm <sup>-3</sup> )	$u$ (m sec <sup>-1</sup> )	$\alpha \times 10^3$ (K <sup>-1</sup> )	$\beta_1 \times 10^{12}$ (cm <sup>2</sup> dyn <sup>-1</sup> )	$V_1$	$V^*$ (cm <sup>3</sup> mol <sup>-1</sup> )	$T^*$ (K)	$P_-$	$P^* \times 10^{-7}$ (dyn cm <sup>-2</sup> )	$\beta_s \times 10^{12}$ (cm <sup>2</sup> dyne <sup>-1</sup> )	$C_p$ (J K <sup>-1</sup> mol <sup>-1</sup> )	$\gamma$	$C_v$ (J K <sup>-1</sup> mol <sup>-1</sup> )	$\Gamma$	$P \times 10^{-7}$ (dyn cm <sup>-2</sup> )
0.1	0.9871	1624.2	0.998	52.03	1.2508	75.4263	5273.69	0.00011	910.03	38.40	209.20	1.355	154.40	1.1726	788.11
10	0.9917	1653.3	0.988	49.91	1.2507	75.0828	5188.15	0.01083	923.31	36.89	213.56	1.353	157.86	1.1779	802.00
20	0.9962	1682.1	0.978	47.92	1.2506	74.7548	5107.79	0.02136	936.42	35.48	217.88	1.351	161.30	1.1830	815.82
30	1.0005	1710.1	0.969	46.10	1.2504	74.4432	5032.60	0.03161	949.04	34.18	222.10	1.349	164.66	1.1879	829.26
40	1.0047	1737.3	0.960	44.42	1.2501	74.1463	4961.94	0.04162	961.17	32.98	226.23	1.347	167.95	1.1925	842.30
50	1.0088	1763.9	0.951	42.86	1.2498	73.8632	4895.50	0.05139	972.96	31.86	230.28	1.345	171.19	1.1969	855.08
60	1.0127	1787.7	0.944	41.51	1.2497	73.5837	4829.99	0.06106	982.66	30.90	233.96	1.343	174.16	1.2004	865.87
70	1.0166	1814.9	0.935	40.07	1.2493	73.3321	4772.92	0.07034	995.16	29.86	238.10	1.342	177.46	1.2051	879.47
80	1.0203	1839.3	0.928	38.82	1.2489	73.0817	4715.99	0.07956	1005.54	28.97	241.87	1.340	180.49	1.2088	891.06
90	1.0240	1862.9	0.921	37.67	1.2486	72.8399	4661.40	0.08864	1015.38	28.14	245.54	1.338	183.45	1.2123	902.16
100	1.0275	1885.9	0.914	36.58	1.2483	72.6067	4609.13	0.09758	1024.82	27.36	249.13	1.337	186.35	1.2156	912.92
110	1.0310	1908.1	0.908	35.58	1.2480	72.3805	4558.64	0.10641	1033.69	26.64	252.62	1.335	189.17	1.2187	923.17
120	1.0343	1929.7	0.902	34.63	1.2477	72.1614	4509.87	0.11515	1042.16	25.96	256.04	1.334	191.94	1.2216	933.05
130	1.0376	1950.5	0.896	33.76	1.2475	71.9481	4462.61	0.12381	1050.03	25.33	259.35	1.333	194.62	1.2242	942.40
140	1.0409	1970.5	0.891	32.94	1.2472	71.7398	4416.36	0.13241	1057.30	24.74	262.55	1.331	197.23	1.2267	951.19
150	1.0440	1989.9	0.885	32.17	1.2470	71.5370	4371.35	0.14096	1064.13	24.19	265.68	1.330	199.78	1.2289	959.57
160	1.0471	2008.5	0.880	31.45	1.2468	71.3384	4327.11	0.14949	1070.33	23.67	268.70	1.329	202.25	1.2310	967.38



Table 3.2

Calculated values of excess volume of  
x-toluene + (1-x) o-xylene at 303.15 K

Pressure (MPa)	x = 0.8	x = 0.6	x = 0.4	x = 0.2
0.1	0.0153	0.0213	0.0211	0.0153
10	0.0096	0.0131	0.0116	0.0056
20	0.0081	0.0108	0.0097	0.0050
30	0.0092	0.0109	0.0095	0.0052
40	0.0076	0.0094	0.0086	0.0054
50	0.0056	0.0075	0.0074	0.0054
60	0.0061	0.0065	0.0052	0.0027
70	-0.0007	0.0004	0.0003	-0.0009
80	0.0030	0.0030	0.0019	0.0002
90	0.0042	0.0041	0.0033	0.0021
100	0.0012	0.0022	0.0026	0.0027
110	-0.0014	-0.0667	-0.0723	-0.0779
120	0.0032	0.0031	0.0028	0.0025
130	-0.0032	-0.0029	-0.0025	-0.0020
140	-0.0017	-0.0007	0.0003	0.0015
150	-0.0036	-0.0039	-0.0040	-0.0040
160	-0.0031	-0.0039	-0.0043	-0.0040

Table 3.3

Calculated values of excess volume of  
x-toluene + (1-x) aniline at 303.15 K

Pressure (MPa)	x = 0.8	x = 0.6	x = 0.4	x = 0.2
0.1	0.0047	0.5078	0.6758	0.8121
10	-0.0186	0.2042	0.2843	0.3623
20	-0.0337	-0.0554	-0.0596	-0.0427
30	-0.0410	-0.0573	-0.0560	-0.0308
40	-0.0473	0.1141	0.1849	0.2689
50	-0.0523	-0.0789	-0.0784	-0.0508
60	-0.0534	0.2355	0.3607	0.4939
70	-0.0630	-0.0926	-0.0973	-0.0753
80	-0.0581	-0.0780	-0.0722	-0.0373
90	-0.0583	0.1936	0.3083	0.4359
100	-0.0625	-0.0938	-0.0968	-0.0719
110	-0.0634	-0.1253	-0.1119	-0.0688
120	-0.0591	-0.0829	-0.0784	-0.0445
130	-0.0658	-0.0950	-0.0932	-0.0619
140	-0.0632	-0.0914	-0.0890	-0.0578
150	-0.0638	-0.0921	-0.0902	-0.0597
160	-0.0629	-0.0919	-0.0905	-0.0604

Table 3.4

Experimental and calculated values of density of x-toluene + (1-x) o-xylene at 303.15 K along with percentage deviations

Pressure (MPa)	x = 0.8			x = 0.6			x = 0.4			x = 0.2		
	Expt.	Cal.	% dev.	Expt.	Cal.	% dev.	Expt.	Cal.	% dev.	Expt.	Cal.	% dev.
0.1	0.8605	0.8609	-0.04	0.8605	0.8636	-0.36	0.8605	0.8653	-0.68	0.8605	0.8689	-0.98
10	0.8680	0.8684	-0.05	0.8678	0.8711	-0.37	0.8677	0.8736	-0.69	0.8675	0.8761	-0.98
20	0.8750	0.8755	-0.06	0.8770	0.8780	-0.12	0.8796	0.8805	-0.10	0.8822	0.8828	-0.07
30	0.8816	0.8821	-0.06	0.8834	0.8845	-0.13	0.8859	0.8869	-0.11	0.8884	0.8891	-0.08
40	0.8877	0.8883	-0.06	0.8895	0.8906	-0.13	0.8919	0.8929	-0.11	0.8943	0.8950	-0.08
50	0.8935	0.8941	-0.07	0.8952	0.8964	-0.13	0.8976	0.8985	-0.12	0.8999	0.9006	-0.08
60	0.8990	0.8996	-0.07	0.9006	0.9018	-0.13	0.9028	0.9039	-0.12	0.9052	0.9059	-0.08
70	0.9042	0.9048	-0.07	0.9058	0.9069	-0.13	0.9079	0.9090	-0.12	0.9102	0.9110	-0.09
80	0.9091	0.9097	-0.07	0.9107	0.9118	-0.13	0.9127	0.9139	-0.12	0.9150	0.9158	-0.09
90	0.9138	0.9144	-0.07	0.9154	0.9165	-0.13	0.9174	0.9185	-0.13	0.9196	0.9204	-0.09
100	0.9184	0.9190	-0.07	0.9199	0.9210	-0.12	0.9218	0.9230	-0.13	0.9240	0.9248	-0.09
110	0.9227	0.9233	-0.06	0.9242	0.9253	-0.12	0.9261	0.9272	-0.13	0.9282	0.9291	-0.09
120	0.9269	0.9275	-0.06	0.9283	0.9295	-0.12	0.9302	0.9314	-0.13	0.9323	0.9332	-0.09
130	0.9309	0.9315	-0.06	0.9323	0.9334	-0.12	0.9341	0.9353	-0.13	0.9363	0.9371	-0.09
140	0.9348	0.9353	-0.06	0.9362	0.9373	-0.12	0.9380	0.9392	-0.13	0.9401	0.9409	-0.09
150	0.9385	0.9391	-0.06	0.9399	0.9410	-0.11	0.9417	0.9429	-0.13	0.9437	0.9446	-0.09
160	0.9422	0.9427	-0.06	0.9436	0.9446	-0.11	0.9453	0.9465	-0.13	0.9473	0.9482	-0.09

Table 3.5

Experimental and calculated values of density of x-toluene + (1-x) aniline at 303.15 K along with percentage deviations

Pressure (MPa)	x = 0.8			x = 0.6			x = 0.4			x = 0.2		
	Cal.		% dev.	Cal.		% dev.	Cal.		% dev.	Cal.		% dev.
	Expt.	Cal.		Expt.	Cal.		Expt.	Cal.		Expt.	Cal.	
0.1	0.8654	0.9061	-2.34	0.9136	0.9520	-4.21	0.9462	1.0032	-6.02	0.9789	1.0573	-8.01
10	0.8924	0.9137	-2.40	0.9198	0.9619	-4.57	0.9518	1.0137	-6.50	0.9841	1.0681	-8.53
20	0.8989	0.9208	-2.44	0.9258	0.9710	-4.88	0.9572	1.0234	-6.92	0.9892	1.0783	-9.01
30	0.9051	0.9274	-2.46	0.9314	0.9773	-4.93	0.9624	1.0294	-6.97	0.9941	1.0838	-9.03
40	0.9110	0.9336	-2.48	0.9368	0.9815	-4.77	0.9673	1.0324	-6.72	0.9988	1.0855	-8.68
50	0.9165	0.9394	-2.49	0.9419	0.9889	-4.99	0.9721	1.0405	-7.04	1.0033	1.0942	-9.06
60	0.9218	0.9448	-2.50	0.9468	0.9911	-4.67	0.9767	1.0408	-6.57	1.0077	1.0927	-8.43
70	0.9268	0.9500	-2.51	0.9515	0.9994	-5.03	0.9810	1.0506	-7.09	1.0120	1.1039	-9.08
80	0.9316	0.9550	-2.51	0.9561	1.0042	-5.04	0.9853	1.0553	-7.10	1.0161	1.1082	-9.07
90	0.9362	0.9597	-2.51	0.9604	1.0059	-4.74	0.9894	1.0554	-6.67	1.0201	1.1067	-8.50
100	0.9406	0.9642	-2.51	0.9646	1.0134	-5.05	0.9934	1.0643	-7.14	1.0240	1.1170	-9.09
110	0.9449	0.9686	-2.51	0.9687	1.0176	-5.06	0.9972	1.0684	-7.14	1.0277	1.1209	-9.07
120	0.949	0.9728	-2.50	0.9726	1.0218	-5.06	1.0010	1.0725	-7.14	1.0314	1.1249	-9.06
130	0.9530	0.9768	-2.50	0.9764	1.0258	-5.06	1.0046	1.0764	-7.15	1.0350	1.1288	-9.06
140	0.9568	0.9807	-2.49	0.9801	1.0296	-5.06	1.0081	1.0802	-7.15	1.0385	1.1325	-9.06
150	0.9606	0.9844	-2.49	0.9836	1.0334	-5.06	1.0116	1.0840	-7.16	1.0419	1.1362	-9.05
160	0.9642	0.9881	-2.48	0.9871	1.0371	-5.06	1.0149	1.0876	-7.16	1.0452	1.1398	-9.05

Table 3.6  
Experimental and calculated values of thermal expansion coefficient of x-toluene + (1-x) o-xylene  
at 303.15 K along with percentage deviations

Pressure (MPa)	$\alpha \times 10^3 \text{ (K}^{-1}\text{)}$											
	x = 0.8			x = 0.6			x = 0.4			x = 0.2		
	Expt.	Cal.	% dev.	Expt.	Cal.	% dev.	Expt.	Cal.	% dev.	Expt.	Cal.	% dev.
0.1	1.172	1.171	0.10	1.167	1.166	0.10	1.164	1.161	0.24	1.159	1.156	0.31
10	1.146	1.146	0.00	1.142	1.141	0.08	1.139	1.137	0.22	1.136	1.132	0.32
20	1.124	1.125	-0.07	1.120	1.121	-0.07	1.116	1.116	-0.05	1.112	1.112	-0.04
30	1.105	1.105	0.03	1.101	1.101	-0.05	1.097	1.097	0.00	1.093	1.093	-0.03
40	1.087	1.087	-0.02	1.083	1.083	-0.02	1.079	1.079	0.00	1.075	1.075	0.00
50	1.071	1.071	0.01	1.068	1.067	0.05	1.064	1.064	0.01	1.060	1.060	0.00
60	1.056	1.056	0.02	1.052	1.052	0.07	1.049	1.047	0.14	1.046	1.044	0.25
70	1.043	1.044	-0.03	1.041	1.040	0.09	1.037	1.037	-0.01	1.033	1.033	-0.04
80	1.031	1.031	-0.03	1.028	1.028	0.03	1.025	1.024	0.03	1.021	1.021	-0.02
90	1.019	1.020	-0.04	1.017	1.017	-0.01	1.013	1.014	-0.03	1.011	1.011	0.00
100	1.010	1.010	-0.02	1.007	1.007	-0.05	1.004	1.004	-0.02	1.002	1.002	0.03
110	0.999	0.999	-0.04	0.996	0.997	-0.07	0.994	0.994	0.05	0.992	0.991	0.03
120	0.989	0.990	-0.08	0.987	0.987	-0.05	0.984	0.985	-0.04	0.982	0.982	-0.02
130	0.980	0.981	0.08	0.978	0.979	-0.09	0.976	0.976	-0.06	0.973	0.974	-0.04
140	0.973	0.972	0.02	0.970	0.970	0.01	0.967	0.968	-0.07	0.966	0.966	0.02
150	0.965	0.964	0.05	0.963	0.962	0.03	0.961	0.960	0.04	0.958	0.958	0.01
160	0.957	0.957	0.02	0.955	0.955	0.03	0.953	0.952	0.09	0.951	0.950	0.06

Table 3.7

Experimental and calculated values of thermal expansion coefficient of x-toluene + (1-x) aniline at 303.15 K along with percentage deviations

Pressure (MPa)	x = 0.8			x = 0.6			x = 0.4			x = 0.2		
	Expt.	Cal.	% dev.	Expt.	Cal.	% dev.	Expt.	Cal.	% dev.	Expt.	Cal.	% dev.
0.1	1.141	1.142	-0.14	1.107	1.140	-2.97	1.068	1.115	-4.37	1.030	1.088	-5.64
10	1.120	1.120	0.06	1.088	1.102	-1.30	1.063	1.074	-2.03	1.017	1.046	-2.83
20	1.101	1.100	0.14	1.070	1.070	0.06	1.038	1.039	-0.13	1.004	1.009	-0.43
30	1.084	1.081	0.19	1.056	1.063	0.23	1.025	1.025	0.01	0.993	0.997	-0.39
40	1.067	1.065	0.12	1.041	1.049	-0.78	1.013	1.027	-1.45	0.983	1.005	-2.17
50	1.052	1.050	0.20	1.028	1.025	0.29	1.001	1.000	0.07	0.974	0.976	-0.19
60	1.038	1.037	0.14	1.016	1.031	-1.44	0.991	1.015	-2.39	0.964	0.998	-3.59
70	1.027	1.025	0.18	1.005	1.002	0.27	0.980	0.979	0.10	0.955	0.957	-0.20
80	1.015	1.013	0.17	0.995	0.991	0.33	0.972	0.970	0.18	0.947	0.949	-0.20
90	1.005	1.002	0.21	0.985	0.987	-1.25	0.964	0.983	-1.97	0.940	0.969	-3.08
100	0.994	0.993	0.13	0.974	0.973	0.19	0.954	0.953	0.19	0.931	0.933	-0.15
110	0.984	0.983	0.13	0.966	0.964	0.23	0.946	0.945	0.13	0.924	0.926	-0.22
120	0.975	0.974	0.11	0.958	0.956	0.21	0.938	0.938	0.07	0.917	0.920	-0.26
130	0.968	0.966	0.20	0.951	0.948	0.23	0.932	0.931	0.10	0.911	0.914	-0.24
140	0.959	0.958	0.14	0.944	0.940	0.34	0.925	0.924	0.17	0.906	0.907	-0.13
150	0.952	0.950	0.22	0.937	0.934	0.32	0.919	0.917	0.19	0.900	0.901	-0.16
160	0.945	0.943	0.15	0.930	0.927	0.29	0.913	0.911	0.15	0.894	0.896	-0.18

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## **Chapter-4**

Pressure dependent studies of internal pressure and pseudo-Gruneisen parameter for binary liquid mixtures

## Introduction:

Internal pressure has been found to be a very important parameter in the theory of liquid state. In liquid state, cohesive forces are of prime importance. Different liquid systems differ essentially in their relative degree of cohesion and this cohesion creates a pressure directed inward of magnitude between  $10^3$  to  $10^4$  atm. Thus, the internal pressure which is the resultant of forces of attraction and repulsion between the constituents in the liquid medium provides the estimate of pressure directed inward by cohesion. The internal pressure of liquids is highly useful in understanding molecular interactions, internal structure and the clustering phenomenon.

Pioneer attempts by Hildebrand et al<sup>(1)</sup>, Barton<sup>(2)</sup>, Rosseinsky<sup>(3)</sup>, Berkowitz et al<sup>(4)</sup> and Suryanarayana<sup>(5)</sup> demonstrate the significance of internal pressure as a fundamental property of the liquid state and its correlation with other thermodynamic properties.

Internal pressure has been a subject of active interest during recent past. Successful attempts have been made by several investigators<sup>(6-10)</sup> to determine the internal pressure of binary liquid mixtures. Theoretical deduction of internal pressure of binary liquid mixtures was carried out by Subrahmanyam et al<sup>(6-8)</sup> using Flory's statistical theory.

In the theory of lattice dynamics, the extent of anharmonicity of the lattice is characterized by a parameter called Grüneisen parameter denoted by  $\Gamma$ . This dimensionless parameter is basically a diagnostic parameter and has been found to be a very useful tool for investigating the thermodynamic and other anharmonic behaviour of the solid crystalline lattices<sup>(11-15)</sup>.

For the first time Knopoff and Shapiro<sup>(16)</sup> extended the study of this parameter to liquids also. It has been found that Grüneisen parameter is an equally suitable parameter to investigate the internal structure, clustering phenomenon and other quasi-crystalline properties of liquids.



For liquids, the pseudo-counterpart of the term  $\Gamma$  is defined as,

$$\Gamma = \alpha u^2 / C_P \quad \dots\dots\dots(4.1)$$

Where  $u$  is the velocity of sound,  $\alpha$  the coefficient of thermal expansion and  $C_P$  is the heat capacity at constant pressure.

$$\text{Using the relation, } u^2 = \frac{1}{\beta_s \cdot \rho}$$

$$\text{and, } \gamma = \frac{C_P}{C_V} = \frac{\beta_T}{\beta_S}, \text{ we get}$$

$$\Gamma = \frac{\alpha V}{\beta_T C_V} = \frac{\gamma - 1}{\alpha T} \quad \dots\dots\dots(4.2)$$

where  $V$  is the molar volume.

Several workers<sup>(17-18)</sup> have evaluated Grüneisen parameter in binary liquid mixtures and this parameter has been used to study the intermolecular interactions between the molecules.

In the present work, we have computed internal pressure and pseudo- Grüneisen parameter of two binary mixtures namely toluene + o-xylene and toluene + aniline using pressure-dependent Flory's statistical theory. As far as our knowledge is concerned, no work has, so far, been done on the pressure dependent properties of binary mixtures on the basis of Flory theory. This is our first attempt to apply Flory theory for evaluating internal pressure and pseudo-Grüneisen parameter of binary liquid mixtures at elevated pressures.

#### Theory:

Equations (2.32) and (2.41) have been utilized to obtain the internal pressure and pseudo- Grüneisen parameter respectively of liquid mixtures on the basis of Flory's statistical theory as discussed in chapter – 2 of this thesis.

## Results and Discussion:

The two binary liquid mixtures under consideration for the present investigation are: toluene + o-xylene and toluene + aniline. Internal pressure and pseudo-Grüneisen parameter of the two above mentioned liquid mixtures have been evaluated at elevated pressures ranging from 0.1 MPa to 160 MPa and at temperature of 303.15 K for four different mole fractions. Flory's statistical theory has been employed to compute the internal pressure and pseudo-Grüneisen parameter of the binary mixtures at the above mentioned conditions. Experimental data of pure components and binary mixtures have been taken from the literature<sup>(19)</sup>. Wherever experimental values are not available, these are obtained with the help of well-known empirical relations recently<sup>(20-22)</sup> proposed using the experimental values of density and ultrasonic velocity available in the literature<sup>(19)</sup>. Theoretical results, thus obtained, have been compared with the experimental findings. The experimental and calculated values of internal pressure, along with percentage deviations at different mole fractions for toluene + o-xylene and toluene + aniline, are reported in tables 4.1 and 4.2 respectively. Similarly, the experimental and theoretical values of pseudo-Grüneisen parameter, along with percentage deviations, for the aforementioned mixtures are reported in tables- 4.3 and 4.4 respectively.

A careful study of tables 4.1 and 4.2 show that the calculated values of internal pressure show the same trend as observed experimentally. In all the cases, the values of internal pressure increase with the increase in pressure. The values of internal pressure increase with decrease in mole fraction of toluene in both the liquid mixtures at all pressures. The percentage deviations between computed and observed values of internal pressure are below one percent for toluene + o-xylene and less than two percent for toluene + aniline.

But, the calculated values of pseudo-Grüneisen parameter show opposite trend than that observed experimentally for both the liquid mixtures.

Table 4.1

Experimental and calculated values of internal pressure of x-toluene + (1-x) o-xylene at 303.15 K along with percentage deviations

Pressure (MPa)	$P_i$ (dyn cm <sup>-3</sup> )											
	x = 0.8			x = 0.6			x = 0.4			x = 0.2		
	Expt.	Cal.	% dev.	Expt.	Cal.	% dev.	Expt.	Cal.	% dev.	Expt.	Cal.	% dev.
0.1	359.48	361.14	-0.46	364.17	366.10	-0.53	367.49	370.93	-0.94	371.62	375.64	-1.08
10	374.58	375.04	-0.12	378.43	380.05	-0.43	381.78	384.93	-0.84	385.42	389.67	-1.10
20	387.78	387.26	0.13	392.32	392.06	0.07	396.83	396.73	0.02	401.41	401.26	0.04
30	398.71	399.36	-0.16	404.27	404.12	0.04	408.25	408.73	-0.12	413.34	413.20	0.03
40	410.96	410.96	0.00	416.16	416.24	-0.02	420.94	421.36	-0.10	426.13	426.33	-0.05
50	421.22	421.60	-0.09	425.70	426.69	-0.23	431.21	431.62	-0.10	436.20	436.40	-0.05
60	431.66	432.14	-0.11	436.88	438.21	-0.31	441.79	444.09	-0.52	445.76	449.78	-0.90
70	439.74	439.48	0.06	443.23	444.77	-0.35	449.90	449.88	0.01	455.35	454.82	0.12
80	449.10	448.66	0.10	453.08	453.76	-0.15	458.05	458.69	-0.14	463.78	463.45	0.07
90	456.53	455.96	0.12	461.21	461.09	0.03	466.54	466.05	0.10	470.87	470.84	0.01
100	462.85	462.62	0.05	467.94	467.16	0.17	471.79	471.56	0.05	475.25	475.80	-0.12
110	470.95	470.22	0.15	476.36	475.10	0.27	478.96	479.81	-0.18	483.81	484.35	-0.11
120	478.81	477.28	0.32	483.09	482.11	0.20	487.58	486.77	0.17	491.77	491.27	0.10
130	484.78	483.25	0.31	489.69	487.96	0.35	493.69	492.51	0.24	497.76	496.89	0.18
140	489.43	489.83	-0.08	494.12	494.22	-0.02	499.92	498.45	0.29	502.26	502.53	-0.05
150	494.50	495.48	-0.20	499.29	499.76	-0.09	503.30	503.88	-0.12	507.77	507.86	-0.02
160	500.26	500.51	-0.05	504.99	505.43	-0.09	508.59	510.16	-0.31	513.61	514.73	-0.22

Table 4.2

Experimental and calculated values of internal pressure of x-toluene + (1-x) aniline at 303.15 K along with percentage deviations

Pressure (MPa)	x = 0.8				x = 0.6				x = 0.4				x = 0.2			
	Expt.		% dev.		Expt.		% dev.		Expt.		% dev.		Expt.		% dev.	
	Cal.	Cal.	Cal.	Cal.	Cal.	Cal.	Cal.	Cal.	Cal.	Cal.	Cal.	Cal.	Cal.	Cal.	Cal.	Cal.
0.1	389.87	393.05	-0.82	427.09	429.44	-0.55	474.70	471.96	0.58	530.35	533.72	-0.63	518.81	518.81	0.00	2.18
10	401.87	406.49	-1.15	440.00	444.43	-1.01	486.05	487.08	-0.21	540.93	547.95	-1.28	533.72	533.72	0.00	1.33
20	413.72	418.64	-1.19	452.47	458.18	-1.26	498.10	501.19	-0.62	551.76	557.95	-1.11	547.95	547.95	0.00	0.69
30	425.26	430.46	-1.22	462.07	469.46	-1.60	507.37	511.72	-0.86	561.43	567.48	-1.06	557.48	557.48	0.00	0.70
40	437.33	441.24	-0.89	472.86	478.03	-1.09	517.60	518.73	-0.22	569.01	572.70	-0.65	562.70	562.70	0.00	1.11
50	446.97	451.79	-1.08	482.61	489.95	-1.52	527.01	531.04	-0.76	576.92	582.52	-0.96	575.25	575.25	0.00	0.29
60	457.40	460.96	-0.78	491.89	495.44	-0.72	534.76	534.18	0.11	587.42	591.28	-0.65	587.42	587.42	0.00	1.97
70	465.13	469.30	-0.90	500.65	507.13	-1.29	544.63	547.73	-0.57	595.45	599.28	-0.63	591.28	591.28	0.00	0.70
80	474.56	478.41	-0.81	508.44	515.87	-1.46	551.03	555.93	-0.89	601.74	607.98	-1.03	603.86	603.86	0.00	0.49
90	481.27	485.66	-0.91	516.62	522.09	-1.06	556.43	561.59	-0.93	607.98	612.58	-0.75	612.58	612.58	0.00	0.68
100	489.89	492.88	-0.61	525.79	530.21	-0.84	566.00	570.05	-0.72	616.68	623.11	-1.04	623.11	623.11	0.00	0.67
110	497.23	500.02	-0.56	531.97	537.15	-0.97	573.25	576.69	-0.60	623.11	629.46	-1.03	629.46	629.46	0.00	0.69
120	504.65	506.98	-0.46	539.26	543.91	-0.86	581.34	583.18	-0.32	630.44	634.12	-0.59	634.12	634.12	0.00	0.87
130	509.04	513.03	-0.78	544.35	551.46	-1.31	585.96	591.52	-0.95	634.93	639.06	-0.64	639.06	639.06	0.00	0.13
140	516.90	519.68	-0.54	548.96	556.18	-1.32	591.14	594.93	-0.64	639.06	641.03	-0.31	641.03	641.03	0.00	0.47
150	520.93	525.31	-0.84	554.92	561.65	-1.21	644.93	650.18	-0.68	644.93	650.09	-0.02	650.09	650.09	0.00	-0.60
160	526.72	529.70	-0.57	560.07	566.04	-1.07	650.09	654.55	-0.68	650.09	654.55	-0.68	654.55	654.55	0.00	0.73

Table 4.3

Experimental and calculated values of pseudo-Gruneisen parameter of *x*-toluene + (1-*x*) *o*-xylene at 303.15 K along with percentage deviations

Pressure (MPa)	$x = 0.8$			$x = 0.6$			$x = 0.4$			$x = 0.2$		
	Expt.		% dev.	Expt.		% dev.	Expt.		% dev.	Expt.		% dev.
	Cal.	Cal.		Cal.	Cal.		Cal.	Cal.		Cal.	Cal.	
0.1	1.1774	1.1772	0.02	1.1825	1.1780	0.38	1.1860	1.1791	0.59	1.1905	1.1803	0.85
10	1.1922	1.1094	6.95	1.1964	1.1113	7.12	1.2001	1.1134	7.23	1.2041	1.1156	7.35
20	1.2046	1.0443	13.31	1.2060	1.0468	13.20	1.2063	1.0495	13.00	1.2066	1.0522	12.80
30	1.2144	0.9639	18.98	1.2167	0.9871	18.87	1.2165	0.9604	18.59	1.2172	0.9936	18.36
40	1.2252	0.9272	24.33	1.2271	0.9318	24.07	1.2275	0.9363	23.73	1.2282	0.9408	23.40
50	1.2340	0.8729	29.26	1.2351	0.8778	28.93	1.2362	0.8826	28.61	1.2366	0.8873	28.25
60	1.2427	0.8217	33.87	1.2443	0.8672	30.31	1.2449	0.8754	29.68	1.2443	0.8834	29.00
70	1.2492	0.7685	38.48	1.2494	0.8401	32.76	1.2514	0.8461	32.39	1.2520	0.8519	31.96
80	1.2567	0.7208	42.64	1.2573	0.7271	42.17	1.2578	0.7331	41.71	1.2586	0.7391	41.28
90	1.2626	0.6724	46.75	1.2637	0.6791	46.28	1.2645	0.6856	45.78	1.2641	0.6919	45.27
100	1.2676	0.6249	50.70	1.2689	0.6527	48.58	1.2686	0.6577	48.16	1.2675	0.6625	47.78
110	1.2738	0.5812	54.37	1.2753	0.6337	50.31	1.2741	0.6398	49.78	1.2740	0.6458	49.31
120	1.2798	0.5364	57.93	1.2804	0.5455	57.40	1.2805	0.5523	56.87	1.2799	0.5589	56.33
130	1.2840	0.4953	61.44	1.2854	0.5024	60.92	1.2851	0.5092	60.38	1.2844	0.5158	59.84
140	1.2880	0.4549	64.68	1.2888	0.4795	62.80	1.2897	0.4855	62.36	1.2878	0.4913	61.85
150	1.2919	0.4142	67.94	1.2927	0.4209	67.44	1.2925	0.4273	66.94	1.2919	0.4335	66.44
160	1.2962	0.3736	71.18	1.2969	0.3975	69.35	1.2964	0.4059	68.69	1.2962	0.4140	68.06

Table 4.4

Experimental and calculated values of pseudo-Gruneisen parameter of x-toluene + (1-x) aniline at 303.15 K along with percentage deviations

Pressure (MPa)	x = 0.8				x = 0.6				x = 0.4				x = 0.2			
	Expt.		Cal.		Expt.		Cal.		Expt.		Cal.		Expt.		Cal.	
			% dev.				% dev.				% dev.				% dev.	
0.1	1.1708	1.1656	0.45	1.1634	1.1615	0.16	1.1552	1.1617	1.1552	0.56	1.1491	1.1661	1.1491	-1.47	1.1661	-1.47
10	1.1816	1.1043	6.54	1.1742	1.1052	5.88	1.1637	1.1098	4.63	1.1559	1.1176	3.31	1.1559	1.1176	3.31	1.1559
20	1.1918	1.0451	12.31	1.1842	1.0516	11.2	1.1725	1.0606	9.55	1.1627	1.0718	7.82	1.1627	1.0718	7.82	1.1627
30	1.2015	0.9996	17.64	1.1916	1.0004	16.05	1.1790	1.0131	14.07	1.1685	1.0273	12.08	1.1685	1.0273	12.08	1.1685
40	1.2114	0.9352	22.72	1.1998	0.9499	20.83	1.1860	0.9657	18.57	1.1728	0.9826	16.22	1.1728	0.9826	16.22	1.1728
50	1.2190	0.8856	27.35	1.207	0.904	25.1	1.1923	0.9230	22.59	1.1773	0.9425	19.95	1.1773	0.9425	19.95	1.1773
60	1.2271	0.8359	31.88	1.2186	0.8733	28.04	1.1978	0.8871	25.9	1.1833	0.902	23.77	1.1833	0.902	23.77	1.1833
70	1.2323	0.7874	36.13	1.2198	0.8474	30.53	1.2036	0.8593	28.6	1.1877	0.8723	26.56	1.1877	0.8723	26.56	1.1877
80	1.2388	0.7423	40.13	1.2252	0.7696	37.18	1.2076	0.7964	34.05	1.1910	0.8227	30.92	1.1910	0.8227	30.92	1.1910
90	1.2447	0.6964	44.05	1.2307	0.7289	40.77	1.2109	0.7598	37.26	1.1942	0.7902	33.83	1.1942	0.7902	33.83	1.1942
100	1.2509	0.6524	47.84	1.2368	0.6982	43.55	1.2168	0.7250	40.42	1.1987	0.7512	37.33	1.1987	0.7512	37.33	1.1987
110	1.2561	0.6100	51.43	1.2409	0.6704	45.97	1.2211	0.6945	43.12	1.2020	0.7162	40.25	1.2020	0.7162	40.25	1.2020
120	1.2612	0.5690	54.89	1.2456	0.6054	51.4	1.2259	0.6404	47.76	1.2057	0.6741	44.09	1.2057	0.6741	44.09	1.2057
130	1.2643	0.5279	58.25	1.2489	0.5707	54.3	1.2286	0.6096	50.38	1.2078	0.6470	48.48	1.2078	0.6470	48.48	1.2078
140	1.2697	0.4893	61.46	1.2519	0.5396	56.9	1.2316	0.5739	53.41	1.2097	0.6069	57.00	1.2097	0.6069	57.00	1.2097
150	1.2725	0.4502	64.62	1.2557	0.4914	60.87	1.2345	0.5308	57.00	1.2125	0.5687	53.10	1.2125	0.5687	53.10	1.2125
160	1.2764	0.4100	67.88	1.259	0.4613	63.36	1.2375	0.4996	59.63	1.2150	0.5364	55.85	1.2150	0.5364	55.85	1.2150

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## **Chapter-5**

Estimation of pressure dependent thermodynamic properties ( $C_p$ ,  $C_p^E$ ,  $C_v$ ,  $\gamma$ ) of binary liquid mixtures



## Introduction:

Heat capacity measurements have been found<sup>(1,2)</sup> to be useful in the investigation of change of liquid structure taking place during mixing. Heat capacity is a second – order thermodynamic quantity and it seems to be unique amongst thermodynamic quantities as an indicator to changes of structure (i.e. order) or non-randomness in pure liquids and mixtures<sup>(3)</sup> during the mixing process. Thus, order–destruction and order –creation processes in mixtures can also be studied through determination of the corresponding excess quantity. The negative excess heat capacity ( $C_P^E$ ) corresponds to order-destruction process whereas for order-creation process, the excess heat capacity ( $C_P^E$ ) is positive.

Heat capacity measurements were carried out by Patterson et al<sup>(4,5)</sup> and Ahluwalia et al<sup>(6,7)</sup> during recent years. Flory's statistical theory has been utilized to estimate  $C_P$  and  $C_P^E$  in various binary liquids. Despite the large number of measurements on binary liquid mixtures, few studies have included pressure as an experimental variable, and in only very few cases these studies have been done at pressures other than atmospheric. In the present work, we have applied Flory's statistical theory at elevated pressures.

## Theory:

In the present chapter  $C_P$ ,  $C_P^E$ ,  $C_V$  and  $\gamma$  of binary liquid mixtures have been calculated with the help of Flory's statistical theory at elevated pressures through the eqs. (2.33), (2.36), (2.40) and (2.39) respectively. The reduced and characteristic parameters, which are used in computation, have been deduced by the procedure mentioned in chapter–2. Parameters for pure components are obtained from table 3.1. Thermal expansion coefficient and isothermal compressibility of pure components are obtained from empirical relations<sup>(9-11)</sup> recently proposed

and isentropic compressibility is obtained from the thermodynamic relation,

$\beta_s = (u^2 \rho)^{-1}$ , where the values of ultrasonic velocity and density are taken from the literature<sup>(8)</sup>. Heat capacities at constant pressure are obtained from the relation,

$$C_P = \frac{\alpha^2 TV}{\beta_T - \beta_S}$$

### Results and Discussion:

The two binary liquid mixtures taken for the present investigation are : toluene + o-xylene and toluene + aniline. Heat capacity at constant pressure, heat capacity at constant volume and heat capacities ratio have been evaluated using Flory's statistical theory at elevated pressures at 303.15 K. The calculated values for both the mixtures are compared with the experimental ones, and percentage deviations were calculated. Excess heat capacities of the liquid mixtures have also been reported. Since for the above mentioned liquid mixtures, the experimental values of  $C_P$ ,  $C_V$  and  $\gamma$  were not available, we have adopted an indirect method to get these values. The well-known thermodynamic relation is,

$$\beta_T - \beta_S = \frac{\alpha^2 TV}{C_P} \quad \dots\dots\dots(5.1)$$

Rearranging this equation, we get

$$C_P = \frac{\alpha^2 TV}{\beta_T - \beta_S} \quad \dots\dots\dots(5.2)$$

so, we can write

$$C_{P(\text{exp.})} = \frac{\alpha^2_{(\text{exp.})} TV_{(\text{exp.})}}{\beta_{T(\text{exp.})} - \beta_{S(\text{exp.})}} \quad \dots\dots\dots(5.3)$$

where, isentropic compressibility

$$\beta_{S(\text{exp.})} = \frac{1}{u^2_{(\text{exp.})} \rho_{(\text{exp.})}} \quad \dots\dots\dots(5.4)$$

The experimental values of ultrasonic velocity and density are taken from the literature<sup>(8)</sup>. Thermal expansion coefficient and isothermal compressibility are obtained from the empirical relations<sup>(9-11)</sup> using experimental values of ultrasonic velocity and density at temperature T as,

$$\alpha_{(\text{exp})} = \frac{75.6 * 10^{-3}}{T^{1/9} u^{1/2}_{(\text{exp.})} \rho^{1/3}_{(\text{exp.})}} \quad \dots\dots(5.5)$$

$$\text{and,} \quad \beta_T(\text{exp.}) = \frac{17.1 * 10^{-4}}{T^{4/9} u^2_{(\text{exp.})} \rho^{4/3}_{(\text{exp.})}} \quad \dots\dots(5.6)$$

Experimental heat capacities ratio is obtained from

$$\gamma_{(\text{exp.})} = \frac{\beta_T(\text{exp.})}{\beta_S(\text{exp.})} \quad \dots\dots(5.7)$$

and experimental heat capacity at constant volume as,

$$C_{V(\text{exp.})} = \frac{C_{P(\text{exp.})}}{\gamma_{(\text{exp.})}} \quad \dots\dots(5.8)$$

Tables 5.1 and 5.2 enlist the calculated and experimental values of heat capacity at constant pressure along with the percentage deviations for the systems toluene + o-xylene and toluene + aniline respectively. Tables 5.1(a) and 5.2(a) record the values of excess heat capacity for mixtures toluene + o-xylene and toluene + aniline respectively. The experimental and calculated values of heat capacity at constant volume along with percentage deviations are reported in tables 5.3 and 5.4 respectively for toluene + o-xylene and toluene + aniline. In tables 5.5 and 5.6, the experimental and calculated values of heat capacities ratio along with percentage deviations at four mole fractions are reported respectively for toluene + o-xylene and toluene + aniline.

A close perusal of tables 5.1, 5.2, 5.3, 5.4, 5.5, and 5.6 reveals that calculated values of  $C_p$ ,  $C_v$ , and  $\gamma$  for both the mixtures show the same trend as experimental one. The values of  $C_p^E$  are, in general, negative for both liquid mixtures. A close observation of tables 5.1 and 5.2 show that  $C_p$  increases as pressure increases at every mole fraction and at a constant pressure,  $C_p$  increases as the mole fraction of toluene in the mixtures decreases. For toluene + o-xylene, the maximum deviation is nearly five percent but in most cases it is less than one percent. But for toluene + aniline, the maximum percentage deviation is about ten. In this case percentage deviation increases as mole fraction of toluene in the mixtures decreases.

From tables 5.3 and 5.4, it is evident that variation in  $C_v$  with pressure and also with mole fraction show, in general, the same trend as  $C_p$  i.e.  $C_v$  increases when pressure is increased or the composition of toluene in the mixtures is decreased. Percentage deviations for  $C_v$  are greater than that for  $C_p$ . Percentage deviation increases as pressure increases for toluene + o-xylene but for toluene + aniline, this variation is not so straight forward but some what complex. A careful study of tables 5.5 and 5.6 reveals that value of  $\gamma$  decrease as pressure increases at every mole fraction for both the mixtures. But at a constant pressure when mole fraction is changed, an interesting result is seen for both the mixtures. The value of  $\gamma$  decreases as content of toluene decreases in the mixtures upto a certain pressure but it increases as toluene decreases after this certain pressure. This pressure is 30 MPa for toluene + o-xylene and 70 MPa for toluene + aniline. For both the mixtures percentage deviation increases with pressure and maximum percentage deviation is upto twenty for both the mixtures.

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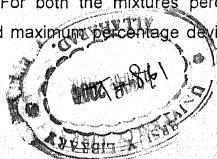


Table 5.1

Experimental and calculated values of heat capacity at constant pressure of x-toluene + (1-x) o-xylene at 303.15 K along with percentage deviations

Pressure (MPa)	x = 0.8			x = 0.6			x = 0.4			x = 0.2		
	Cal.		% dev.	Cal.		% dev.	Cal.		% dev.	Cal.		% dev.
	Expt.	Cal.		Expt.	Cal.		Expt.	Cal.		Expt.	Cal.	
0.1	157.68	158.23	-0.35	163.74	164.32	-0.35	169.46	170.40	-0.56	175.49	176.49	-0.57
10	164.62	164.81	-0.11	170.52	171.07	-0.27	176.51	177.34	-0.47	182.58	183.60	-0.56
20	170.91	170.81	0.06	177.49	177.17	0.01	183.50	183.52	-0.01	189.89	189.88	0.01
30	176.47	176.59	-0.13	183.18	183.18	0.00	189.49	189.67	-0.10	196.48	196.17	0.01
40	182.30	182.34	-0.02	189.06	189.13	-0.04	195.75	195.91	-0.09	202.62	202.70	-0.04
50	187.51	187.65	-0.07	194.21	194.52	-0.16	201.23	201.39	-0.08	208.48	208.26	-0.04
60	192.70	192.86	-0.09	199.73	194.51	2.61	206.73	201.38	2.59	213.53	208.26	2.47
70	197.22	197.17	0.02	203.91	194.51	4.61	211.49	201.38	4.78	218.62	208.25	4.83
80	202.01	201.92	0.04	208.96	209.16	-0.10	216.22	216.41	-0.09	223.74	223.66	0.04
90	206.26	206.14	0.06	213.51	213.51	0.00	220.98	220.87	0.05	228.24	228.24	0.00
100	210.20	210.16	0.02	217.66	213.51	1.91	224.85	220.87	1.77	231.97	228.25	1.61
110	214.54	214.38	0.08	222.20	213.42	3.95	229.18	220.78	3.66	236.79	228.15	3.65
120	218.78	218.43	0.16	226.27	226.05	0.10	233.86	233.66	0.08	241.41	241.28	0.05
130	222.53	222.18	0.16	230.28	229.86	0.18	237.84	237.55	0.12	245.47	245.24	0.09
140	225.94	226.05	-0.05	233.72	229.86	1.65	241.83	237.55	1.77	249.12	245.25	1.55
150	229.42	229.66	-0.11	237.32	237.44	-0.05	245.08	245.23	-0.06	253.00	253.02	-0.01
160	233.04	233.11	-0.03	241.02	237.44	1.49	248.78	245.23	1.43	256.94	253.02	1.53

Table 5.2

Experimental and calculated values of heat capacity at constant pressure of x-toluene + (1-x) aniline at 303.15 K along with percentage deviations

Pressure (MPa)	x = 0.8			x = 0.6			x = 0.4			x = 0.2		
	Cal.		% dev.	Cal.		% dev.	Cal.		% dev.	Cal.		% dev.
	Expt.	Cal.		Expt.	Cal.		Expt.	Cal.		Expt.	Cal.	
0.1	165.54	163.59	1.18	180.49	175.45	2.63	198.00	187.05	5.53	218.46	198.63	9.08
10	171.45	169.55	1.11	186.37	180.77	3.01	203.74	191.85	5.83	223.97	202.95	9.39
20	177.25	175.14	1.19	192.36	185.81	3.40	209.61	196.49	6.26	229.51	207.18	9.73
30	182.87	180.56	1.26	197.49	190.94	3.31	214.67	201.32	6.22	234.68	211.72	9.78
40	188.55	185.67	1.53	202.87	185.98	3.40	219.93	206.19	6.25	239.25	216.42	9.54
50	193.51	190.65	1.48	207.91	200.53	3.55	224.92	210.43	6.44	243.87	220.35	9.65
60	198.62	195.24	1.70	212.77	202.35	4.90	229.42	213.14	7.10	249.11	223.93	10.11
70	202.99	198.58	1.68	217.46	203.64	6.35	234.43	215.10	8.25	253.68	226.57	10.69
80	207.73	204.08	1.76	221.85	213.50	3.76	238.51	222.95	6.53	257.78	232.41	9.84
90	211.76	208.09	1.73	226.80	217.75	3.78	242.82	227.25	6.22	261.83	236.77	9.57
100	216.21	212.05	1.92	230.95	218.85	5.24	247.13	228.91	7.37	266.47	239.00	10.31
110	220.81	215.97	1.97	234.83	220.20	6.23	251.33	230.98	8.10	270.51	241.79	10.62
120	224.41	219.81	2.05	238.95	228.84	4.28	255.70	237.89	6.97	274.75	246.96	10.12
130	227.74	223.41	1.90	242.51	232.35	4.19	259.20	241.32	6.90	278.27	250.32	10.05
140	231.87	227.13	2.05	245.93	233.64	5.00	262.82	243.25	7.45	281.69	252.89	10.23
150	235.07	230.59	1.91	249.65	239.32	4.14	266.37	248.08	6.87	285.51	256.86	10.03
160	238.67	233.75	2.06	253.16	240.52	4.99	269.97	249.89	7.44	289.14	259.28	10.33

Table 5.1(a)

Calculated values of excess heat  
capacity of x-toluene + (1-x) o-xylene  
at 303.15 K

Pressure (MPa)	x = 0.8	x = 0.6	x = 0.4	x = 0.2
0.1	0.0044	0.0053	0.0052	0.0044
10	0.0001	-0.0010	-0.0023	-0.0033
20	-0.0009	-0.0025	-0.0035	-0.0037
30	0.0002	-0.0023	-0.0036	-0.0034
40	-0.0021	-0.0051	-0.0060	-0.0043
50	-0.0038	-0.0066	-0.0068	-0.0040
60	-0.0050	-0.0104	-0.0117	-0.0087
70	-0.0108	-0.0148	-0.0150	-0.0112
80	-0.0065	-0.0115	-0.0127	-0.0097
90	-0.0053	-0.0105	-0.0114	-0.0078
100	-0.0078	-0.0112	-0.0108	-0.0062
110	-0.0115	-0.0926	-0.0995	-0.1017
120	-0.0059	-0.0110	-0.0114	-0.0068
130	-0.0137	-0.0162	-0.0178	-0.0123
140	-0.0114	-0.0147	-0.0135	-0.0074
150	-0.0136	-0.0164	-0.0186	-0.0141
160	-0.0143	-0.0207	-0.0212	-0.0158

Table 5.2 (a)

Calculated values of excess heat  
capacity of x-toluene + (1-x) aniline  
at 303.15 K

Pressure (MPa)	x = 0.8	x = 0.6	x = 0.4	x = 0.2
0.1	0.0293	0.4850	0.6746	0.8375
10	0.0092	0.2251	0.3146	0.3957
20	-0.0055	-0.0130	-0.0174	-0.0150
30	-0.0140	-0.0175	-0.0167	-0.0045
40	-0.0220	0.1538	0.2358	0.3250
50	-0.0290	-0.0454	-0.0463	-0.0301
60	-0.0323	0.2939	0.4480	0.6094
70	-0.0446	-0.0670	-0.7455	-0.0636
80	-0.0414	-0.0532	-0.0477	-0.0195
90	-0.0436	0.2661	0.4169	0.5813
100	-0.0504	-0.0778	-0.0836	-0.0665
110	-0.0535	-0.1187	-0.1045	-0.0638
120	-0.0502	-0.0653	-0.0650	-0.0341
130	-0.0602	-0.0877	-0.0871	-0.0590
140	-0.0588	-0.0853	-0.0837	-0.0547
150	-0.0613	-0.0888	-0.8778	-0.0590
160	-0.0618	-0.0909	-0.0905	-0.0615

Table 5.3

Experimental and calculated values of heat capacity at constant volume of x-toluene + (1-x) o-xylene at 303.15 K along with percentage deviations

Pressure (MPa)	$C_v$ (J K <sup>-1</sup> mol <sup>-1</sup> )											
	x = 0.8			x = 0.6								
	Expt.	Cal.	% dev.	Expt.	Cal.	% dev.						
x = 0.4												
x = 0.2												
	Expt.	Cal.	% dev.	Expt.	Cal.	% dev.						
0.1	111.17	111.80	-0.39	115.45	116.01	-0.49	119.48	120.43	-0.80	123.73	124.86	-0.91
10	116.40	118.95	-2.19	120.63	123.56	-2.42	124.79	128.17	-2.71	129.07	132.78	-2.87
20	121.17	125.96	-3.95	125.72	130.69	-3.96	130.32	135.42	-3.91	135.00	140.16	-3.82
30	125.42	132.89	-5.95	130.29	137.78	-5.75	134.90	142.67	-5.76	139.79	147.56	-5.56
40	129.87	139.66	-7.54	134.77	144.82	-7.46	139.67	149.98	-7.39	144.70	155.14	-7.21
50	133.87	146.21	-9.22	138.74	151.49	-9.19	143.88	156.77	-9.96	148.98	162.06	-8.78
60	137.86	152.70	-10.77	142.97	152.38	-6.58	148.11	157.58	-6.39	153.11	162.77	-6.31
70	141.36	158.61	-12.20	146.24	153.77	-5.15	151.80	159.08	-4.79	157.19	164.38	-4.57
80	145.06	164.80	-13.61	150.14	170.54	-13.59	155.46	176.27	-13.38	161.01	182.01	-13.04
90	148.37	170.67	-15.03	153.67	176.55	-14.89	159.16	182.44	-14.63	164.52	188.32	-14.47
100	151.45	176.41	-16.48	156.91	178.03	-13.46	162.20	184.02	-13.45	167.48	190.01	-13.46
110	154.82	182.28	-17.74	160.43	179.13	-11.66	165.59	185.10	-11.78	171.22	191.07	-11.59
120	158.12	188.05	-18.93	163.62	194.33	-18.77	169.21	200.60	-18.55	174.81	206.86	-18.34
130	161.06	193.65	-20.24	166.75	200.05	-19.97	172.34	206.44	-19.79	178.00	212.83	-19.57
140	163.75	199.32	-21.72	169.48	201.46	-18.87	175.47	207.93	-18.50	180.89	214.40	-18.53
150	166.50	204.85	-23.04	172.32	211.48	-22.73	178.06	218.10	-22.49	183.95	224.72	-22.16
160	169.34	210.31	-24.19	175.23	212.95	-21.52	180.98	219.50	-21.28	187.05	226.06	-20.86



Table 5.4

Experimental and calculated values of heat capacity at constant volume of x-toluene + (1-x) aniline at 303.15 K along with percentage deviations

Pressure (MPa)	$C_v$ (J K <sup>-1</sup> mol <sup>-1</sup> )					
	x = 0.8			x = 0.6		
	Expt.	Cal.	% dev.	Expt.	Cal.	% dev.
x = 0.4						
	Expt.	Cal.	% dev.	Expt.	Cal.	% dev.
x = 0.2						
	Expt.	Cal.	% dev.	Expt.	Cal.	% dev.
0.1	117.83	116.54	1.1	129.61	125.21	3.39
10	122.35	123.33	-0.8	134.35	132.03	1.73
20	126.8	129.88	-2.43	138.97	138.57	0.29
30	131.12	136.33	-3.98	142.96	144.71	-1.22
40	135.48	142.57	-5.23	147.14	150.49	-2.28
50	139.33	148.72	-6.74	151.07	156.54	-3.62
60	143.28	154.61	-7.91	154.87	158.96	-2.64
70	146.7	160.36	-9.31	158.54	161.94	-2.15
80	150.39	166.2	-10.51	162	173.4	-7.04
90	153.55	171.74	-11.85	165.5	178.44	-7.82
100	157.03	177.26	-12.88	169.14	181.49	-7.3
110	160.25	182.74	-14.04	172.23	184.13	-6.91
120	163.46	188.2	-15.13	175.49	194.69	-10.95
130	166.12	193.5	-16.48	178.33	199.6	-11.93
140	169.36	198.88	-17.43	181.08	202.49	-11.82
150	171.93	204.12	-18.72	184.04	210.1	-14.16
160	174.77	209.22	-19.7	186.95	212.92	-13.95
				201.1	219.58	-9.19
				217.51	226.51	-4.05
				214.55	222.32	-3.62
				211.45	216.72	-2.5
				208.65	212.28	-1.74
				205.77	207.89	-1.03
				202.35	201.21	0.57
				199.09	197.12	0.99
				192.1	187.94	2.17
				188.79	180.83	4.22
				185.13	175.92	4.97
				180.97	172.31	4.78
				168.41	164.41	0.45
				165.15	164.41	0.45
				161.23	158.52	1.68
				157.11	153.12	2.54
				153.13	147.29	3.81
				148.56	140.93	5.14
				144.09	134.31	6.79
				160.79	143.46	10.77

Table 5.5

Experimental and calculated values of heat capacities ratio of x-toluene + (1-x) o-xylene at 303.15 K along with percentage deviations

Pressure (MPa)	x = 0.8			x = 0.6			x = 0.4			x = 0.2		
	Cal.		% dev.	Cal.		% dev.	Cal.		% dev.	Cal.		% dev.
	Expt.	Cal.		Expt.	Cal.		Expt.	Cal.		Expt.	Cal.	
0.1	1.418	1.418	0.03	1.418	1.416	0.14	1.418	1.415	0.24	1.418	1.414	0.34
10	1.414	1.386	2.04	1.414	1.385	2.1	1.414	1.384	2.16	1.415	1.383	2.24
20	1.410	1.356	3.85	1.409	1.356	3.82	1.408	1.355	3.75	1.407	1.355	3.69
30	1.407	1.330	5.5	1.406	1.330	5.44	1.405	1.329	5.36	1.403	1.329	5.27
40	1.404	1.306	6.99	1.403	1.306	6.9	1.402	1.306	6.8	1.400	1.307	6.69
50	1.401	1.283	8.37	1.400	1.284	8.27	1.399	1.285	8.15	1.397	1.285	8.03
60	1.398	1.263	9.64	1.397	1.277	8.63	1.396	1.278	8.44	1.395	1.280	8.26
70	1.395	1.243	10.9	1.394	1.265	9.28	1.393	1.266	9.14	1.392	1.267	8.99
80	1.393	1.225	12.02	1.392	1.227	11.88	1.391	1.228	11.72	1.390	1.229	11.57
90	1.390	1.208	13.12	1.389	1.209	12.96	1.388	1.211	12.8	1.387	1.212	12.64
100	1.388	1.191	14.17	1.387	1.199	13.55	1.386	1.200	13.41	1.385	1.201	13.28
110	1.386	1.176	15.13	1.385	1.191	13.98	1.384	1.193	13.82	1.383	1.194	13.66
120	1.384	1.162	16.05	1.383	1.163	15.89	1.382	1.165	15.71	1.381	1.166	15.54
130	1.382	1.147	16.96	1.381	1.149	16.79	1.380	1.151	16.62	1.379	1.152	16.44
140	1.380	1.134	17.8	1.379	1.141	17.26	1.378	1.143	17.1	1.377	1.144	16.94
150	1.378	1.121	18.64	1.377	1.123	18.47	1.376	1.124	18.31	1.375	1.126	18.14
160	1.376	1.108	19.46	1.375	1.115	18.93	1.375	1.117	18.73	1.374	1.119	18.52

Table 5.6

Experimental and calculated values of heat capacities ratio of  $x$ -toluene +  $(1-x)$  aniline  
at 303.15 K along with percentage deviations

Pressure (MPa)	$\gamma$						$x = 0.4$						$x = 0.2$					
	$x = 0.8$			$x = 0.6$			$x = 0.4$			$x = 0.2$			$x = 0.0$			$x = 0.2$		
	Expt	Cal	% dev.	Expt	Cal	% dev.	Expt	Cal	% dev.	Expt	Cal	% dev.	Expt	Cal	% dev.	Expt	Cal	% dev.
0.1	1.405	1.404	0.09	1.39	1.401	-0.79	1.374	1.393	-1.35	1.359	1.385	-1.9	1.359	1.385	-1.9	1.359	1.385	-1.9
10	1.401	1.375	1.89	1.387	1.369	1.3	1.371	1.361	0.73	1.356	1.354	0.15	1.356	1.354	0.15	1.356	1.354	0.15
20	1.398	1.348	3.54	1.384	1.341	3.12	1.369	1.334	2.54	1.354	1.328	1.94	1.354	1.328	1.94	1.354	1.328	1.94
30	1.395	1.324	5.04	1.381	1.320	4.48	1.366	1.315	3.78	1.352	1.310	3.06	1.352	1.310	3.06	1.352	1.310	3.06
40	1.392	1.302	6.42	1.379	1.302	5.55	1.364	1.301	4.64	1.35	1.299	3.73	1.35	1.299	3.73	1.35	1.299	3.73
50	1.389	1.282	7.7	1.376	1.281	6.92	1.362	1.280	6.02	1.348	1.279	5.11	1.348	1.279	5.11	1.348	1.279	5.11
60	1.386	1.263	8.91	1.374	1.273	7.35	1.36	1.273	6.39	1.346	1.273	5.4	1.346	1.273	5.4	1.346	1.273	5.4
70	1.384	1.245	10.05	1.372	1.258	8.32	1.358	1.255	7.55	1.344	1.253	6.76	1.344	1.253	6.76	1.344	1.253	6.76
80	1.381	1.228	11.11	1.369	1.231	10.09	1.356	1.234	8.97	1.342	1.237	7.84	1.342	1.237	7.84	1.342	1.237	7.84
90	1.379	1.212	12.14	1.367	1.220	10.76	1.354	1.226	9.42	1.340	1.232	8.07	1.340	1.232	8.07	1.340	1.232	8.07
100	1.377	1.196	13.11	1.365	1.206	11.68	1.352	1.209	10.55	1.338	1.212	9.42	1.338	1.212	9.42	1.338	1.212	9.42
120	1.373	1.168	14.92	1.362	1.175	13.68	1.349	1.182	12.99	1.335	1.188	11.08	1.335	1.188	11.08	1.335	1.188	11.08
130	1.371	1.155	15.78	1.36	1.164	14.4	1.347	1.172	12.99	1.334	1.179	11.58	1.334	1.179	11.58	1.334	1.179	11.58
140	1.369	1.142	16.58	1.358	1.154	15.04	1.345	1.161	13.73	1.332	1.167	12.41	1.332	1.167	12.41	1.332	1.167	12.41
150	1.367	1.130	17.38	1.357	1.139	16.03	1.344	1.148	14.61	1.331	1.155	13.18	1.331	1.155	13.18	1.331	1.155	13.18
160	1.366	1.117	18.18	1.355	1.130	16.63	1.342	1.138	15.23	1.329	1.146	13.82	1.329	1.146	13.82	1.329	1.146	13.82

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## **Chapter-6**

Theoretical evaluation of ultrasonic velocity, isothermal compressibility and isentropic compressibility of liquid mixtures at elevated pressures.

## Introduction:

Ultrasonic velocity has been a subject of active interest during the recent past as it plays an important role in the investigation of structure and intermolecular interactions between components of liquid mixtures. Ultrasonic propagation parameters (ultrasonic velocity, absorption, adiabatic compressibility etc.) and thermodynamic parameters (isothermal compressibility, thermal expansion coefficient, heat capacities, heat capacities ratio etc.) are very important in understanding the physico-chemical behavior of the liquid state. In addition, ultrasonic velocity has been proved to be an important property to test the validity of liquid state models.

There are certain thermodynamic properties of liquid which are not easily accessible by direct experimentation. Measurement of sound velocity provides a convenient method for determining these thermodynamic properties of liquids. Literature survey<sup>(1-8)</sup> shows that ultrasonic study of liquid mixtures is highly useful in understanding the nature of molecular interactions present in the mixtures. Various successful attempts have been made in the recent past<sup>(9-14)</sup> on theoretical evaluation of ultrasonic velocity and its correlation with other thermodynamic properties in binary liquid mixtures using statistical and semi-empirical theories. But such studies have been limited to binary liquid mixtures at zero pressures. Due to the lack of experimental data on ultrasonic velocity at elevated pressures, such studies could not be extended at elevated pressures. For the first time, Takagi et al<sup>(15-18)</sup> have carried out accurate experimental measurements of ultrasonic velocity and related thermodynamic properties of few binary liquid mixtures at elevated pressures over a wide range of temperatures. Although of late<sup>(19-27)</sup>, some work on ultrasonic speed and thermodynamic parameters has been carried out, however, to our knowledge, comparatively limited work is available at elevated pressures. In the present work, an attempt has been made to evaluate theoretically ultrasonic velocity at elevated pressures

using Flory's theory. The theoretical method employed has already been detailed out earlier.

Isentropic compressibility ( $\beta_s$ ) has been widely used to study the molecular interactions through its excess value<sup>(39-41)</sup>. On the other hand, it can also be used to deduce other useful thermodynamic properties e. g. isothermal compressibility ( $\beta_T$ ), heat capacities ratio ( $\gamma$ ), internal pressure ( $P_i$ ) etc. These properties are accessible from isentropic compressibility ( $\beta_s$ ) provided the values of thermal expansion coefficient ( $\alpha$ ) and heat capacity at constant pressure ( $C_p$ ) are known. Isentropic compressibility is a very complex quantity. The more fundamental thermodynamic quantity is the isothermal rather than the isentropic compressibility. The isothermal compressibility,  $\beta_T = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T$ , is a directly measurable thermodynamic quantity. It is the key parameter in molecular thermodynamics of fluid phase equilibria. The isothermal compressibility of a liquid or liquid mixture can be obtained directly from pressure-volume measurements, or indirectly from the isentropic compressibility ( $\beta_s$ ) according to the relation

$$\beta_T = \beta_s + \frac{\alpha^2 TV}{C_p}.$$

where  $\alpha$  is the thermal expansion coefficient,  $T$  the temperature,  $V$  the volume and  $C_p$  is the heat capacity at constant pressure.

Isothermal compressibility has been widely evaluated by many workers<sup>(28-32)</sup> for pure liquids but very limited attempts<sup>(33-36)</sup> have been made to evaluate isothermal compressibility for liquid mixtures. In the present work, Flory's statistical theory has been employed for the theoretical evaluation of ultrasonic velocity, isothermal and isentropic compressibilities of binary mixtures at elevated pressures.

## Theory:

Equations (2.46), (2.31) and (2.38) have been used to obtain ultrasonic velocity, isothermal compressibility and isentropic compressibility respectively of the liquid mixtures under the present consideration with the help of Flory's statistical theory at elevated pressures. The reduced and characteristic parameters, which are used in computation, have been deduced by the method discussed in chapter -2.

## Results and Discussion:

The two binary liquid mixtures taken for the present investigation are: toluene + o-xylene and toluene + aniline. The values of ultrasonic velocity, isothermal compressibility and isentropic compressibility of the binary mixtures have been evaluated with the help of Flory's statistical theory at elevated pressures ranging from 0.1 MPa to 160 MPa and at constant temperature of 303.15 K for four different mole fractions. Parameters of the pure components are obtained from table-3.1. Thermal expansion coefficient and isothermal compressibility of pure components are obtained from the empirical relations<sup>(37,38)</sup> where the values of ultrasonic velocity and density are taken from the literature<sup>(16)</sup>.

The calculated values of the properties for both the mixtures are compared with the experimental ones and percentage deviations were calculated. Experimental values of ultrasonic velocity for both the mixtures are taken from the literature<sup>(16)</sup>. Since the experimental values of isothermal and isentropic compressibilities were not available, we have adopted an indirect method to get these values. Using well-known thermodynamic relation,

$$\beta_s = \frac{1}{u^2 \rho} \quad \text{---(6.1)}$$

we can write 
$$\beta_{s(\text{exp.})} = \frac{1}{u^2_{(\text{exp.})} \rho_{(\text{exp.})}} \quad \text{----(6.2)}$$



The experimental values of isothermal compressibility are obtained using empirical relation<sup>(37,38)</sup>.

$$\beta_{T(\text{exp.})} = \frac{17.1 \cdot 10^{-4}}{T^{4/9} u^2_{(\text{exp.})} \rho^{4/3}_{(\text{exp.})}} \quad \text{---(6.3)}$$

The experimental values of ultrasonic velocity and density of liquid mixtures, employed in the above eqs. (6.2) and (6.3), are taken from the literature<sup>(16)</sup>.

The experimental and calculated values of ultrasonic velocity along with the percentage deviations at different mole fractions for toluene + o-xylene and toluene + aniline are reported in tables 6.1 and 6.2 respectively. Tables 6.3 and 6.4 contain the experimental and calculated values of isothermal compressibility with percentage deviations at different mole fractions for toluene + o-xylene and toluene + aniline respectively. Similarly, the experimental and calculated values of isentropic compressibility along with the percentage deviations at different mole fractions for toluene + o-xylene and toluene + aniline are reported in tables 6.5 and 6.6 respectively.

A close perusal of tables 6.1, 6.2, 6.3, 6.4, 6.5 and 6.6 reveals that the calculated values of  $u$ ,  $\beta_T$  and  $\beta_s$  for both the mixtures show the same trend as experimental one. A close perusal of tables 6.1 and 6.2 shows that ultrasonic velocity for both the mixtures increases as pressure increases at each mole fraction, and at a constant pressure, ultrasonic velocity increases as the concentration of toluene in the mixtures decreases. For both the mixtures, percentage deviation increases as pressure increases with maximum deviation of seventeen percent.

From tables 6.3 and 6.4, it is evident that computed values of isothermal compressibility for both the mixtures decrease as the pressure increases, and at a constant pressure it decreases as the mole fraction of toluene in the mixtures decreases. The percentage deviation increases as the pressure increases, and maximum percentage deviation for both the mixtures is nearly fifteen percent.

A close observation of tables 6.5 and 6.6 reveals that the variation of isentropic compressibility with pressure and also with mole fraction shows the same trend as isothermal compressibility i.e. it decreases as pressure increases or as the concentration of toluene in the mixtures decreases. In this case also, the percentage deviation increases as pressure increases but it is greater than that as observed in the case of isothermal compressibility. Here, the maximum percentage deviation is nearly forty six percent for toluene + o-xylene and is nearly forty three percent for toluene + aniline.

Table 6.1

Experimental and calculated values of ultrasonic velocity of x-toluene + (1-x) o-xylene at 303.15 K along with percentage deviations

Pressure (MPa)	x = 0.8			x = 0.6			x = 0.4			x = 0.2		
	Expt.	Cal.	% dev.	Expt.	Cal.	% dev.	Expt.	Cal.	% dev.	Expt.	Cal.	% dev.
0.1	1291.5	1294.5	-0.23	1302.7	1303.4	-0.05	1310.6	1312.2	-0.12	1320.4	1320.8	-0.03
10	1342.9	1318.6	1.81	1352.0	1327.6	1.81	1359.8	1336.4	1.72	1368.5	1345.0	1.72
20	1388.9	1339.1	3.59	1397.1	1347.5	3.55	1404.5	1355.7	3.47	1412.0	1363.8	3.41
30	1428.9	1359.5	4.85	1439.2	1367.8	4.96	1445.3	1375.9	4.80	1453.7	1383.7	4.81
40	1471.1	1379.1	6.25	1480.4	1388.5	6.21	1488.1	1397.6	6.08	1496.5	1406.5	6.02
50	1508.3	1396.8	7.39	1515.9	1405.6	7.27	1525.0	1414.3	7.26	1532.8	1422.6	7.19
60	1545.3	1414.3	8.48	1554.3	1432.2	7.86	1562.0	1443.0	7.62	1567.5	1553.5	7.27
70	1576.9	1425.2	9.62	1582.2	1446.2	8.60	1593.4	1455.1	8.68	1601.8	1463.7	8.62
80	1610.7	1440.1	10.59	1616.9	1448.8	10.39	1624.5	1457.2	10.30	1633.3	1465.4	10.28
90	1640.2	1451.2	11.52	1647.7	1459.9	11.40	1655.9	1468.4	11.33	1661.8	1476.5	11.15
100	1667.2	1461.2	12.36	1675.4	1472.7	12.10	1680.6	1479.7	11.95	1684.7	1486.5	11.76
110	1697.4	1473.2	13.21	1706.1	1489.9	12.67	1708.8	1497.6	12.36	1715.5	1505.0	12.27
120	1726.8	1484.2	14.05	1733.2	1492.1	13.91	1739.5	1499.8	13.78	1744.8	1507.1	13.62
130	1752.3	1493.1	14.79	1759.8	1500.7	14.72	1765.1	1508.1	14.56	1770.1	1515.2	14.40
140	1775.1	1503.3	15.31	1782.1	1513.8	15.06	1790.7	1520.3	15.10	1792.4	1526.7	14.82
150	1798.5	1511.8	15.94	1805.6	1518.5	15.90	1810.8	1524.9	15.79	1816.4	1531.0	15.71
160	1823.0	1519.1	16.67	1829.9	1530.1	16.38	1834.3	1537.8	16.16	1840.8	1545.2	16.06

Table 6.2

Experimental and calculated values of ultrasonic velocity of x-toluene + (1-x) aniline  
at 303.15 K along with percentage deviations

Pressure (MPa)	x = 0.8				x = 0.6				x = 0.4				x = 0.2			
	Expt.	Cal.	% dev.	Expt.	Cal.	% dev.	Expt.	% dev.	Expt.	Cal.	% dev.	Expt.	Cal.	% dev.	Expt.	% dev.
0.10	1337.6	1326.0	0.87	1392.0	1352.7	2.82	1459.1	4.58	1535.8	1435.4	6.54	1535.8	1435.4	6.54	1535.8	6.54
10	1380.0	1348.2	2.30	1434.6	1381.6	3.69	1496.4	4.96	1569.5	1465.6	6.82	1569.5	1465.6	6.82	1569.5	6.82
20	1421.4	1367.8	3.77	1475.6	1407.7	4.60	1534.6	5.52	1603.3	1494.3	6.80	1603.3	1494.3	6.80	1603.3	6.80
30	1461.4	1386.9	5.10	1510.0	1424.8	5.64	1566.8	6.51	1634.5	1506.8	7.81	1634.5	1506.8	7.81	1634.5	7.81
40	1501.8	1404.0	6.51	1546.3	1433.5	7.30	1600.4	8.25	1661.5	1505.2	9.41	1661.5	1505.2	9.41	1661.5	9.41
50	1536.5	1420.8	7.53	1580.0	1455.5	7.88	1632.0	8.58	1688.8	1529.9	9.41	1688.8	1529.9	9.41	1688.8	9.41
60	1572.3	1434.8	8.75	1612.3	1499.5	9.48	1690.1	10.23	1747.8	1516.6	11.84	1747.8	1516.6	11.84	1747.8	11.84
70	1602.2	1447.3	9.67	1648.2	1486.5	9.54	1691.8	10.23	1770.9	1552.6	11.92	1770.9	1552.6	11.92	1770.9	11.92
80	1635.1	1461.5	10.62	1671.9	1493.0	10.70	1716.8	11.12	1770.9	1559.8	11.92	1770.9	1559.8	11.92	1770.9	11.92
90	1662.3	1472.0	11.45	1701.0	1495.6	12.07	1739.8	12.39	1794.2	1564.2	13.38	1794.2	1564.2	13.38	1794.2	13.38
100	1692.9	1482.7	12.42	1731.6	1515.5	12.48	1770.0	12.65	1821.5	1578.1	13.36	1821.5	1578.1	13.36	1821.5	13.36
110	1720.7	1493.3	13.22	1756.4	1527.5	13.03	1795.8	13.34	1844.7	1586.1	14.02	1844.7	1586.1	14.02	1844.7	14.02
120	1748.4	1503.6	14.00	1783.0	1532.2	14.07	1822.8	14.32	1869.2	1592.2	14.82	1869.2	1592.2	14.82	1869.2	14.82
130	1770.2	1512.3	14.57	1805.4	1543.0	14.54	1843.6	14.67	1888.8	1604.3	15.06	1888.8	1604.3	15.06	1888.8	15.06
140	1798.2	1522.2	15.35	1826.8	1551.2	15.09	1865.2	15.39	1907.7	1606.1	15.81	1907.7	1606.1	15.81	1907.7	15.81
150	1819.0	1530.3	15.87	1850.4	1556.5	15.98	1886.3	16.05	1929.3	1611.3	16.48	1929.3	1611.3	16.48	1929.3	16.48
160	1842.8	1536.0	16.65	1872.4	1563.5	16.50	1907.8	16.58	1949.6	1616.6	17.08	1949.6	1616.6	17.08	1949.6	17.08

Table 6.3

Experimental and calculated values of isothermal compressibility of x-toluene + (1-x) o-xylene at 303.15 K along with percentage deviations

Pressure (MPa)	$\beta_t$ ( $\text{cm}^2 \text{dyn}^{-1}$ )					$x = 0.6$					$x = 0.4$					$x = 0.2$				
	$x = 0.8$		% dev.		$\beta_t$	$x = 0.6$		% dev.			$x = 0.4$		% dev.			$x = 0.2$		% dev.		
	Expt.	Cal.				Expt.	Cal.			Expt.	Cal.				Expt.	Cal.				
0.10	90.82	98.28	0.54		97.13	96.54	0.61			95.96	94.86	1.15			94.54	93.25	1.36			
10	90.35	91.76	-1.56		89.16	90.19	-1.15			88.16	88.69	-0.59			87.06	87.26	-0.22			
20	83.56	86.38	-3.38		82.34	85.03	-3.27			81.15	83.74	-3.19			79.98	82.51	-3.17			
30	76.17	81.55	-4.33		76.84	80.34	-4.56			75.91	79.19	-4.32			74.75	78.09	-4.47			
40	73.07	77.28	-5.76		71.96	76.06	-5.7			70.97	74.9	-5.54			69.91	73.8	-5.56			
50	68.91	73.58	-6.77		68.04	72.5	-6.55			67.01	71.48	-6.67			66.09	70.51	-6.68			
60	65.12	70.19	-7.79		64.21	69.01	-7.49			63.37	67.9	-7.15			62.71	66.85	-6.6			
70	62.05	67.65	-9.01		61.49	66.69	-8.45			60.44	65.78	-8.82			59.61	64.91	-8.9			
80	59.05	64.94	-9.98		58.46	64.08	-9.62			57.44	63.26	-9.57			56.93	62.49	-9.77			
90	56.55	62.72	-10.91		55.91	61.9	-10.72			55.2	61.13	-10.76			54.63	60.4	-10.57			
100	54.37	60.72	-11.67		53.72	60.04	-11.75			53.24	59.39	-11.55			52.82	58.78	-11.29			
110	52.13	58.69	-12.59		51.49	58.01	-12.66			51.18	57.36	-12.06			50.63	56.74	-12.08			
120	50.06	56.85	-13.56		49.59	56.21	-13.35			49.1	55.6	-13.24			48.65	55.03	-13.1			
130	48.34	55.25	-14.3		47.83	54.65	-14.28			47.42	54.09	-14.08			47.01	53.56	-13.94			
140	46.84	53.65	-14.53		46.38	53.13	-14.54			45.82	52.63	-14.86			45.6	52.16	-14.39			
150	45.39	52.23	-15.08		44.94	51.75	-15.14			44.58	51.29	-15.06			44.17	50.85	-15.12			
160	43.95	50.95	-15.93		43.53	50.42	-15.82			43.22	49.91	-15.49			42.79	49.44	-15.53			

Table 6.4

Experimental and calculated values of isothermal compressibility of x-toluene + (1-x) aniline at 303.15 K along with percentage deviations

Pressure (MPa)	x = 0.8			x = 0.6			x = 0.4			x = 0.2		
	Expt.		% dev.	Expt.		% dev.	Expt.		% dev.	Expt.		% dev.
	Cal.	Cal.		Cal.	Cal.		Cal.	Cal.		Cal.	Cal.	
0.1	88.69	86.11	0.65	78.54	80.44	-2.42	68.22	71.62	-4.99	58.85	63.56	-8.01
10	82.46	82.77	-0.38	73.28	74.57	-1.77	64.35	66.40	-3.19	55.95	59.02	-5.5
20	76.97	78.27	-1.69	68.67	69.70	-1.5	60.72	62.01	-2.12	53.25	55.14	-3.56
30	72.15	74.24	-2.9	65.04	66.50	-2.24	57.84	59.52	-2.92	50.90	53.25	-4.62
40	67.74	70.77	-4.48	61.55	64.57	-4.90	55.06	58.44	-6.14	48.95	52.83	-7.94
50	64.19	67.61	-5.33	58.53	61.14	-4.47	52.6	55.27	-5.07	47.09	49.93	-6.03
60	60.83	64.92	-6.72	55.82	60.30	-8.03	50.52	55.29	-9.45	45.12	50.65	-12.26
70	58.16	62.55	-7.54	53.38	56.94	-6.66	48.35	51.8	-7.12	43.49	47.09	-8.27
80	55.46	60.2	-8.55	51.24	55.01	-7.34	46.68	50.24	-7.61	42.11	45.86	-8.91
90	53.31	58.27	-9.3	49.21	54.23	-10.21	45.21	50.01	-10.63	40.81	46.09	-12.92
100	51.08	56.44	-10.5	47.21	51.81	-9.76	43.45	47.53	-9.47	39.40	43.58	-10.63
110	49.14	54.72	-11.35	45.63	50.36	-10.38	41.99	46.34	-10.36	38.22	42.62	-11.49
120	47.32	53.11	-12.23	44.04	49.00	-11.27	40.55	45.19	-11.44	37.05	41.66	-12.43
130	45.91	51.68	-12.59	42.73	47.67	-11.55	39.45	43.99	-11.51	36.12	40.59	-12.37
140	44.25	50.26	-13.58	41.53	46.57	-12.16	38.36	43.14	-12.45	35.25	39.94	-13.31
150	43.02	49.00	-13.91	40.28	45.50	-12.97	37.34	42.22	-13.08	34.31	39.17	-14.14
160	41.71	47.93	-14.91	39.15	44.56	-13.81	36.34	41.41	-13.94	33.46	38.46	-14.94

Table 6.5

Experimental and calculated values of isentropic compressibility of x-toluene + (1-x) o-xylene at 303.15 K along with percentage deviations

Pressure (MPa)	x = 0.8			x = 0.6			x = 0.4			x = 0.2		
	Expt.		% dev.	Expt.		% dev.	Expt.		% dev.	Expt.		% dev.
	Cal.	Cal.		Cal.	Cal.		Cal.	Cal.		Cal.	Cal.	
0.1	69.67	69.32	0.51	68.48	68.16	0.47	67.66	67.04	0.91	66.66	65.97	1.02
10	63.88	66.23	-3.67	63.04	65.14	-3.33	62.33	64.10	-2.83	61.55	63.10	-2.52
20	59.24	63.70	-7.52	58.42	62.72	-7.37	57.64	61.79	-7.21	56.86	60.90	-7.12
30	55.56	61.33	-10.40	54.65	60.43	-10.57	54.04	59.57	-10.23	53.26	58.74	-10.28
40	52.05	59.19	-13.71	51.30	58.24	-13.54	50.63	57.34	-13.24	49.93	56.48	-13.12
50	49.20	57.33	-16.53	48.61	56.46	-16.16	47.91	55.64	-16.14	47.30	54.86	-15.99
60	46.58	55.57	-19.30	45.96	54.07	-17.63	45.40	53.13	-17.03	44.96	52.25	-16.20
70	44.48	54.42	-22.34	44.10	52.72	-19.54	43.38	51.96	-19.77	42.82	51.24	-19.66
80	42.40	53.00	-25.01	42.00	52.25	-24.39	41.52	51.53	-24.12	40.97	50.85	-24.13
90	40.68	51.92	-27.65	40.24	51.19	-27.22	39.76	50.50	-27.02	39.38	49.84	-26.97
100	39.18	50.97	-30.11	38.73	50.06	-28.26	38.41	49.48	-28.83	38.13	48.93	-28.33
110	37.62	49.90	-32.67	37.17	48.68	-30.97	36.98	48.09	-32.03	36.61	47.52	-29.81
120	36.18	48.95	-35.27	35.86	48.32	-34.76	35.53	47.74	-34.36	35.23	47.18	-33.91
130	34.98	48.16	-37.65	34.63	47.57	-37.34	34.36	47.01	-35.92	34.09	46.48	-36.36
140	33.95	47.31	-39.34	33.63	46.56	-38.44	33.25	46.07	-38.56	33.11	45.60	-37.72
150	32.94	46.59	-41.44	32.63	46.09	-41.24	32.39	45.61	-40.84	32.12	45.16	-40.62
160	31.94	45.97	-43.93	31.65	45.22	-42.87	31.44	44.68	-42.10	31.15	44.17	-41.79





Table 6.6

Experimental and calculated values of isentropic compressibility of x-toluene + (1-x) aniline at 303.15 K along with percentage deviations

Pressure (MPa)	x = 0.8			x = 0.6			x = 0.4			x = 0.2		
	Expt.		% dev.	Expt.		% dev.	Expt.		% dev.	Expt.		% dev.
	Cal.	Cal.	% dev.	Cal.	Cal.	% dev.	Cal.	Cal.	% dev.	Cal.	Cal.	% dev.
0.10	63.13	62.77	0.56	56.49	57.41	-1.62	49.64	51.43	-3.59	43.31	45.91	-5.99
10	58.84	60.21	-2.32	52.82	54.47	-3.11	46.92	48.77	-3.95	41.25	43.58	-5.66
20	55.06	58.04	-5.42	49.61	51.98	-4.77	44.36	46.48	-4.79	39.33	41.53	-5.60
30	51.73	56.06	-8.36	47.09	50.40	-7.04	42.33	45.27	-6.95	37.65	40.64	-7.92
40	48.67	54.34	-11.65	44.64	49.58	-11.07	40.36	44.92	-11.31	36.27	40.66	-12.12
50	46.22	52.74	-14.11	42.53	47.73	-12.24	38.62	43.18	-11.79	34.95	39.05	-11.73
60	43.88	51.41	-17.16	40.63	47.37	-16.60	37.15	43.44	-16.92	33.53	39.79	-18.67
70	42.03	50.25	-19.56	38.92	45.28	-16.35	35.61	41.27	-15.88	32.37	37.58	-16.11
80	40.15	49.03	-22.11	37.42	44.67	-19.39	34.43	40.70	-18.21	31.38	37.09	-16.18
90	38.66	48.09	-24.40	35.99	44.44	-23.49	33.39	40.78	-22.13	30.45	37.41	-22.83
100	37.09	47.18	-27.18	34.57	42.97	-24.28	32.13	39.30	-22.32	29.43	35.95	-22.13
110	35.74	46.30	-29.54	33.46	42.11	-26.85	31.10	38.65	-24.29	28.59	35.46	-24.02
120	34.47	45.47	-31.91	32.34	41.69	-28.90	30.07	38.23	-27.15	27.75	35.07	-26.37
130	33.49	44.77	-33.68	31.42	40.95	-30.32	29.29	37.54	-28.17	27.08	34.42	-27.09
140	32.32	44.01	-36.16	30.57	40.37	-32.02	28.51	37.17	-30.35	26.46	34.23	-28.36
150	31.46	43.38	-37.87	29.69	39.94	-34.53	27.78	36.79	-32.42	25.79	33.90	-31.46
160	30.54	42.90	-40.45	28.90	39.44	-36.51	27.07	36.38	-34.40	25.17	33.57	-33.37

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## **Chapter-7**

Non-linearity parameter of pure liquids—pressure  
variation studies

## Introduction:

The characteristic, both of medium and the ultrasonic wave propagating through it, is not affected by one another provided the propagating wave has infinitely small amplitude. But, the measurements of the ultrasonic propagation constants e. g. absorption and velocity become unreliable<sup>(1)</sup> when sound waves of finite amplitude propagate through fluids, because several interesting non-linear effects such as acoustic streaming, wave distortion, harmonic generation and sound saturation occur due to unequal attenuation suffered by its different components (the absorption coefficient is proportional to the square of frequency).

These non-linear effects are, mathematically, represented by the non-linear terms in the equation of wave propagation. The non-linear departure of the propagation process is symbolized by the factor  $(B/A)$ , called the non-linearity parameter. If the isentropic equation of state of a medium is represented as a Taylor series and only the quadratic and linear terms are considered, the ratio of the respective coefficients of these terms,  $B/A$ , is used as a parameter to describe the non-linearity of the medium.  $B/A$  of liquids can be obtained from the distortion of finite amplitude waves and the variation of sound velocity with temperature and pressure.

The non-linearity parameter,  $B/A$ , plays a significant role in non-linear acoustics and its determination is of increasing interest in a number of areas ranging from under water acoustics to medical science. From the knowledge of the parameter of non-linearity, one can gain information about some physical properties<sup>(2,4,45)</sup> of the liquids such as internal pressure, intermolecular spacing, acoustic scattering and structural behaviour etc.

A number of experimental and theoretical studies have been performed on the non-linearity parameter of liquids making use of phenomenological<sup>(2-4)</sup> or thermodynamic methods<sup>(5, 6)</sup>. Also, some studies on  $B/A$  have been performed from the view point of theory of liquids<sup>(7)</sup>. The values of  $B/A$  for a series of liquids have long been determined by

many authors using different methods <sup>(8-10)</sup>, but measurement of this parameter for biological media <sup>(11-13)</sup> including living tissues is one of the more recent interest as it can provide important information for the ultrasonic application in biological research related to diagnosis and therapy. It was discovered that the non-linearity parameters of biological media differed strikingly from each other according to their molecular structure, so we can think that  $B/A$  will give some information of the molecular structure of a medium. But we know very little about the relation between them.

Beyer et al <sup>(1,2,8,14)</sup> were the first who presented the theoretical formalism of non-linearity parameter and determined it for a number of organic liquids using sound velocity and other thermodynamic data. Hartmann et al <sup>(15)</sup> discussed the phenomenon (non-linear behaviour of liquids) in view of the potential energy between the molecules by assuming that sound velocity depended on volume only. Endo <sup>(5,7,16,17)</sup> obtained the expression for the non-linearity parameter in the form of a polynomial in terms of the ratio of specific heats and showed that it can be computed from thermodynamic coefficient of sound velocity. Hartmann and Balizer <sup>(15)</sup> have determined the values of non-linearity parameter for n-alkanes using a new equation of state. Theoretical evaluation of these non-linearity parameter for various class of liquids has been done by several workers <sup>(18-20)</sup> Beyer <sup>(1,2,8,14)</sup>, Nomoto <sup>(21)</sup>, Kor et al <sup>(22-24)</sup>, Swamy et al <sup>(18)</sup>, Pandey et al <sup>(25-27,39)</sup> and Sharma <sup>(28-32)</sup> succeeded in computing non-linearity parameter for a number of liquids using thermodynamic approach. Tong et al <sup>(33)</sup> proposed a simplified method for calculating the  $B/A$  values for pure organic liquids making use of Schaaffs equation <sup>(34)</sup> for sound velocity. Recently, using this method, Jugan et al <sup>(35)</sup> and Sanguri et al <sup>(36)</sup> calculated  $B/A$  values of binary liquid mixtures and higher alkanes respectively.

In the present work, computation of  $B/A$  for pure liquids has been carried out at elevated pressures by four different methods. Furthermore, a comparative study of  $B/A$  values obtained from these

methods has also been made in order to review above mentioned approaches, and the merits and demerits of these different methods are discussed in the light of molecular structure and intermolecular interactions.

Thermal expansion coefficient ( $\alpha$ ) and isothermal compressibility ( $\beta_T$ ) of pure liquids are evaluated from recently<sup>(43,46)</sup> proposed relations,

$$\alpha = \frac{75.6 \cdot 10^{-3}}{T^{1/9} u^{1/2} \rho^{1/3}} \quad \text{----(i)}$$

$$\beta_T = \frac{17.1 \cdot 10^{-4}}{T^{4/9} \rho^{4/3} u^2} \quad \text{----(ii)}$$

Adiabatic compressibility ( $\beta_s$ ) is calculated from the thermodynamic relation,

$$\beta_s = \frac{1}{u^2 \rho} \quad \text{----(iii)}$$

The values of ultrasonic velocity and density are taken from the literature<sup>(37)</sup>. Reduced volume is obtained using eq. (2.11).

### Theory:

Ballou<sup>(38)</sup> proposed an empirical rule for the non-linearity parameter using data from Beyer<sup>(8)</sup> on organic liquids, water, liquid metals etc. According to the empirical observation made by Ballou, there is a linear relation between the non-linearity parameter of liquids and reciprocal sound speed as,

$$\frac{B}{A} = -0.5 + \frac{(1.2 \cdot 10^4)}{u} \quad \text{----(7.1)}$$

where  $u$  is the sound velocity expressed in m/sec.

Hartmann<sup>(38)</sup> has shown theoretically the physical basis for the above mentioned empirically observed relation between the non-linearity parameter of liquids and reciprocal sound speed assuming that the inter-

molecular potential energy is the dominant factor in determining sound speed, and its derivatives in liquids. This assumption implies that the thermal pressure contribution to the sound speed is negligible in comparison to the internal pressure contribution. The purpose of the theoretical calculation is to provide physical insight into the proportionality of  $B/A$  with  $1/u$ . The expression for non-linearity parameter,  $B/A$ , due to Hartmann<sup>(38)</sup> is

$$\frac{B}{A} = 2 + \frac{(0.98 \times 10^4)}{u} \quad \text{---(7.2)}$$

This theoretical result was obtained without using any adjustable constants and is in very good agreement with the empirical result.

The non-linear behaviour due to the propagation of finite amplitude wave in fluids can be described by the equation of state  $P = P(\rho, S)$ , where  $P$  is the pressure,  $\rho$  is the density and  $S$  is the entropy of liquid.

Non-linearity parameter,  $B/A$ , can be calculated from the modified thermodynamic equation of state<sup>(14)</sup> for liquids, namely,

$$P = P_0 + A \left( \frac{\rho - \rho_0}{\rho_0} \right) + \frac{B}{2} \left( \frac{\rho - \rho_0}{\rho_0} \right)^2 + \dots \quad \text{---(7.3)}$$

$$\text{where } A = \rho_0 \left( \frac{\partial P}{\partial \rho} \right)_S \bigg|_{\rho = \rho_0} \quad \text{and } B = \rho_0^2 \left( \frac{\partial^2 P}{\partial \rho^2} \right)_S \bigg|_{\rho = \rho_0} \quad \text{---(7.4)}$$

in which subscript 'o' indicates the state without perturbation.

$$\text{Since } u_0^2 = \left( \frac{\partial P}{\partial \rho} \right)_S \bigg|_{\rho = \rho_0} \quad \text{---(7.5)}$$

we get,

$$B = \rho_0^2 \left( \frac{\partial u_0^2}{\partial \rho} \right)_{\rho = \rho_0}$$



$$\text{and, } A = \rho_0 u_0^2$$

therefore,

$$\begin{aligned} \frac{B}{A} &= \frac{\rho_0}{u_0^2} \left( \frac{\partial u_0^2}{\partial \rho} \right) \rho = \rho_0 \\ &= \frac{\rho_0}{u_0^2} \left( \frac{\partial u_0^2}{\partial P} \cdot \frac{\partial P}{\partial \rho} \right)_{\rho = \rho_0} \\ &= \rho_0 \left( \frac{\partial u_0^2}{\partial P} \right) \rho_0 \end{aligned} \quad \text{----(7.6)}$$

In the following deduction subscript 'o' will be omitted but all the variables will take the value at equilibrium.

Thus, we can write from eq. (7.6),

$$\frac{B}{A} = \rho \left( \frac{\partial u^2}{\partial P} \right) \quad \text{----(7.7)}$$

here, it is clear that B/A is related to sound velocity.

Tong et al<sup>(33)</sup> applied Schaaffs equation<sup>(34)</sup> for sound velocity in eq.<sup>(7)</sup> and obtained an equation for B/A as,

$$\frac{B}{A} = J(o) + J(x') \quad \text{----(7.8)}$$

$$\text{where, } J(o) = \left( 1 - \frac{1}{\gamma} \right) \frac{u^2 \rho \beta_T}{\alpha T}$$

on simplification,

$$J(o) = \frac{\gamma - 1}{\alpha T} \quad \text{----(7.9)}$$

$$\text{and } J(x') = \frac{2(3 - 2x')^2}{3(x' - 1)(6 - 5x')} \quad \text{----(7.10)}$$

here,  $\gamma$  is the ratio of specific heats,  $\rho$  the density,  $\alpha$  the thermal expansivity,  $\beta_T$  the isothermal compressibility and  $x'$  is the real volume of a molecule which is the ratio of molar volume,  $V$ , to  $b$ , where  $b$  is the van der Waals constant given by<sup>(34)</sup>

$$b = \frac{M}{\rho} - \frac{\gamma RT}{\rho u^2 - 2P} \left[ \sqrt{\frac{M}{3\gamma RT} \left( u^2 - \frac{2P}{\rho} \right)} + 1 \right] \quad \text{---(7.11)}$$

where M is the molecular weight, R the universal gas constant, u the ultrasonic velocity and P is the pressure.

Because the liquid volume is always larger than the real volume of molecules,  $x'$  is always larger than 1. The expression <sup>(33)</sup> for sound velocity contains a term  $(6-5x')$  in the numerator. Since the ultrasonic velocity can never be negative, the value of  $x'$  can never be more than 1.2. Thus, we have the condition for  $x'$  as

$$1 < x' < 1.2 \quad \text{---(7.12)}$$

From eq. (7.10), it is evident that as the value of  $x'$  tends to 1.2 the value of  $J(x')$  tends to infinity which is an absurd result. Hence, value of  $x'$  plays a very important role in determining B/A values using Tong-Dong method.

General expression for the non-linearity parameter in terms of the acoustical parameters of liquids has been derived using the expression for the sound velocity (u), and introducing the contribution due to isobaric acoustic parameters (K) and the isothermal acoustic parameter (K'). The properties have been deduced with the help of the thermal expansion coefficient ( $\alpha$ ), whose dependence on temperature and pressure may conveniently be utilized to evaluate them.

Moelwyn-Hughes parameter<sup>(40,41)</sup> ( $C_1$ ) is an important thermodynamic quantity in studying the thermodynamics of molecular surface and thermo-acoustical properties. It can be expressed as

$$C_1 = \left( \frac{d \ln K_T}{d \ln V} \right)_T = \left( \frac{13}{3} \right) + (\alpha T)^{-1} + \left( \frac{4\alpha T}{3} \right) \quad \text{---(7.13)}$$

The Sharma parameter ( $S_O$ ) may be expressed as <sup>(30)</sup>

$$S_O = - \left( \frac{X}{2} \right) (3 + 4\alpha T)$$

$$\begin{aligned}
 &= 3S^*(1+2\alpha T)/\tilde{K}_T \\
 &= (1+2\alpha T)(3+4\alpha T)/\tilde{K}_T \quad \text{----(7.14)}
 \end{aligned}$$

where X is the isochoric temperature coefficient of internal pressure,  
i. e.

$$\begin{aligned}
 X &= \left( \frac{d \ln P_{\text{int}}}{d \ln T} \right)_V = \left[ \frac{2(d \ln \alpha)}{(d \ln T)_V} \right] / \tilde{K}_T \\
 &= -2(1+2\alpha T)/(\tilde{V})^{C_1} \quad \text{----(7.15)}
 \end{aligned}$$

$\tilde{K}_T$  is the reduced isothermal bulk modulus, i. e.

$$\tilde{K}_T = (K_T / K^*_T) = (\nu)^{C_1} \quad \text{----(7.16)}$$

$\tilde{V}$  is the reduced specific volume and expressed as,

$$\begin{aligned}
 \tilde{V}(V/V^*) &= (S^*/1+\alpha T)^3 \\
 &= \left[ \left( \frac{\alpha T}{3} / (1+\alpha T) \right) + 1 \right]^3 \quad \text{----(7.17)}
 \end{aligned}$$

$$\text{where } S^* = 1 + \left( \frac{4\alpha T}{3} \right) \quad \text{----(7.18)}$$

$V^*$  and  $K^*_T$  are respectively the hard core specific volume and bulk modulus at absolute zero temperature.

Huggins parameter (F) may be expressed in terms of temperature and pressure derivatives of compressibility<sup>(28)</sup>,

$$\begin{aligned}
 F &= 1 + \frac{2\alpha T}{3} + \left( \frac{d \ln K_T}{d \ln T} \right)_P + \left( \frac{\alpha T}{K_T} \right) \left( \frac{d \ln K_T}{dp} \right)_T \\
 &= 1 + \frac{2\alpha T}{3} + \left( \frac{d \ln K_T}{d \ln T} \right)_V \quad \text{----(7.19)}
 \end{aligned}$$

using eqs. (7.14) and (7.19), the Huggins parameter may be expressed in terms of  $S_0$  as,

$$F + S^* = 2 \left[ 1 + \left( S^* S_2 \right) / \tilde{K}_T \right] = 2 \left[ 1 + \frac{S_0}{3S^*} \right]$$

$$F = 2 \left[ 1 + \left( \frac{S_0}{3S^*} \right) \right] - S^* \quad \text{----(7.20)}$$

The isothermal acoustical parameter ( $K'$ ) is related with the available molar volume ( $V_a$ ) of substance by the expression,

$$\frac{V_a}{V} = (K' + 1)^{-1} = (K'' + K + 1)^{-1} \quad \text{----(7.21)}$$

In this equation the isothermal ( $K'$ ), isochoric ( $K''$ ) and isobaric ( $K$ ) acoustical parameters are given by,

$$K' = \left( \frac{1}{K_T} \right) \left( \frac{d \ln u}{dp} \right)_T$$

$$= - \left( \frac{d \ln u}{d \ln V} \right)_T$$

$$= \frac{1}{2} \left[ 3 + \left\{ S^* (1 + \alpha T) + X \right\} / \alpha T \right] \quad \text{----(7.22)}$$

$$K^{11} = - \left( \frac{d \ln K_T}{d \ln T} \right)_V / 2\alpha T$$

$$= 1 + \left( \frac{X}{2\alpha T} \right) \quad \text{----(7.23)}$$

$$\text{and } K = - \left( \frac{1}{\alpha} \right) \left( \frac{d \ln u}{dT} \right)_p$$

$$= \frac{1}{2} \left[ 1 + S^* (1 + \alpha T) / \alpha T \right] \quad \text{----(7.24)}$$

Beyer's parameter of non-linearity, ( $B/A$ ), which is a particular combination of the temperature and pressure derivatives of the sound velocity may be expressed as<sup>(42)</sup>,

$$\frac{B}{A} = \left( \frac{2Mu^2}{V} \right) \left( \frac{d \ln u}{dp} \right)_T + \left( \frac{2Mu^2 \alpha T}{C_p} \right) \left( \frac{d \ln u}{dT} \right)_p$$

$$= \left( \frac{B}{A} \right)' + \left( \frac{B}{A} \right)'' \quad \text{----(7.25)}$$

$$= 2\gamma K' - 2K(\gamma - 1)$$

$$= 2K + 2\gamma K'' \quad \text{----(7.26)}$$

where  $M$  is the molecular weight,  $\gamma = C_p/C_v$  the heat capacities ratio, and  $C_p$  and  $C_v$  are respectively the isobaric and isochoric heat capacities of the substance.

## Results and Discussion:

The values of non-linearity parameter,  $B/A$ , of pure liquids have been evaluated at elevated pressures and at temperature of 303.15 K with the help of four different methods: Ballou's empirical relation (eq.7.1), Hartmann's theoretically derived relation (eq. 7.2), Tong - Dong method using Schaaffs equation for sound velocity (eq. 7.8) and Sharma's method vide eq. (7.26). The three pure liquids under the present consideration are: toluene, o-xylene and aniline. The different parameters of these liquids, needed for the computation, have been taken from table 3.1. Experimental values of ultrasonic velocity and density are taken from the literature<sup>(37)</sup>.

The calculated values of non-linearity parameter,  $B/A$ , for toluene, o-xylene and aniline, using the above mentioned methods, are reported in tables 7.1, 7.2, and 7.3 respectively. The parameters  $x'$ ,  $J(o)$ ,  $J(x')$  for toluene, o-xylene and aniline used in eq. (7.8) are also reported in the corresponding tables. A close perusal of tables 7.1, 7.2 and 7.3 reveals that the values of  $B/A$  calculated using eqs. (7.1) and (7.2) show a decreasing trend with increase of pressure, whereas the  $B/A$  values obtained from eq. (7.26) increase with increasing pressure. However, the variation in the  $B/A$  values due to this method is very small. Table 7.1 shows that  $B/A$  values for toluene, using eq. (7.8), generally, decrease with increase of pressure. In this case, some values of  $B/A$  are found to be negative. It is because of the value of  $x'$  which is greater than 1.2, the maximum limit of  $x'$  in the Tong-Dong method. In fact, in the Tong-Dong

mehtod, the B/A values are highly sensitive to the values of  $x'$ . It has been noticed that even small changes in values of  $x'$  give very absurd values of B/A. This is mainly due to the factors  $(3-2x')$  in the numerator and  $(6-5x')$  in the denominator in the mathematical expression for  $J(x')$ . in fact, good values of  $J(x')$  or B/A result when  $x'$  lies between 1.10 and 1.14. It is clear from table 7.2 that B/A values for o-xylene decrease with increase of pressure. Table 7.3 reveals that, in the case of aniline, there is a decrease in B/A values with increase of pressure upto 70 MPa, but after this value of pressure, B/A values show an increasing trend with pressure.

Table 7.1

Calculated values of non-linearity parameter of toluene at 303.15 K

Pressure (MPa)	$\rho$	$u$	$x'$	$J(\phi)$	$J(x')$	Tong - Dong		B/A	Ballou's	Hart mann's	B/A	Sharma
		( $\text{m sec}^{-1}$ )										
0.1	0.8580	1285.8	1.212	1.177	-17.052	-15.874		8.833	8.833	9.622	7.450	
10	0.8657	1334.3	1.203	1.191	-67.233	-66.042		8.493	8.493	9.345	7.490	
20	0.8729	1378.7	1.195	1.203	61.738	62.940		8.204	8.204	9.108	7.526	
30	0.8796	1421.6	1.189	1.214	25.071	26.285		7.941	7.941	8.894	7.560	
40	0.8858	1461.3	1.183	1.223	17.391	18.614		7.712	7.712	8.706	7.590	
50	0.8917	1499.9	1.177	1.233	14.002	15.235		7.501	7.501	8.534	7.618	
60	0.8972	1535.1	1.173	1.241	12.212	13.453		7.317	7.317	8.384	7.645	
70	0.9025	1567.0	1.168	1.247	11.131	12.378		7.158	7.158	8.254	7.671	
80	0.9075	1601.0	1.164	1.255	10.317	11.572		6.995	6.995	8.121	7.694	
90	0.9122	1630.3	1.161	1.261	9.796	11.056		6.861	6.861	8.011	7.717	
100	0.9168	1659.3	1.157	1.266	9.396	10.662		6.732	6.732	7.906	7.739	
110	0.9212	1688.0	1.154	1.272	9.084	10.356		6.609	6.609	7.806	7.590	
120	0.9253	1716.1	1.151	1.278	8.840	10.118		6.493	6.493	7.711	7.779	
130	0.9294	1742.0	1.149	1.282	8.658	9.941		6.389	6.389	7.626	7.798	
140	0.9333	1769.2	1.146	1.288	8.503	9.790		6.283	6.283	7.539	7.816	
150	0.9370	1794.0	1.144	1.292	8.387	9.679		6.189	6.189	7.463	7.834	
160	0.9407	1816.0	1.142	1.296	8.301	9.597		6.108	6.108	7.396	7.852	

Table 7.2

Calculated values of non-linearity parameter of o-xylene at 303.15 K

Pressure (MPa)	$\rho$ (gm cm <sup>-3</sup> )	$u$ (m sec <sup>-1</sup> )	$x'$	$J(o)$	$J(x')$	B/A Tong - Dong	B/A Ballou's	B/A Hart mann's	B/A Sharma
0.1	0.8714	1329.5	1.186	1.183	21.239	22.422	8.526	9.371	7.437
10	0.8784	1377.4	1.179	1.196	14.929	16.125	8.212	9.115	7.475
20	0.8850	1418.4	1.173	1.206	12.438	13.644	7.960	8.909	7.511
30	0.8912	1459.8	1.168	1.217	10.969	12.185	7.720	8.713	7.543
40	0.8971	1504.1	1.162	1.228	9.979	11.207	7.478	8.516	7.572
50	0.9026	1539.8	1.158	1.236	9.429	10.665	7.293	8.364	7.600
60	0.9079	1584.0	1.153	1.248	8.950	10.198	7.076	8.187	7.623
70	0.9129	1607.3	1.150	1.251	8.755	10.006	6.966	8.097	7.650
80	0.9176	1638.7	1.147	1.258	8.547	9.805	6.823	7.980	7.674
90	0.9222	1667.7	1.144	1.263	8.398	9.661	6.696	7.876	7.696
100	0.9266	1690.6	1.142	1.267	8.302	9.569	6.598	7.797	7.720
110	0.9308	1721.8	1.139	1.273	8.200	9.473	6.496	7.692	7.739
120	0.9349	1748.9	1.136	1.278	8.132	9.411	6.361	7.604	7.759
130	0.9388	1773.2	1.134	1.282	8.086	9.368	6.267	7.527	7.778
140	0.9426	1797.0	1.132	1.286	8.051	9.338	6.178	7.454	7.797
150	0.9463	1820.4	1.130	1.290	8.027	9.317	6.092	7.383	7.815
160	0.9498	1847.6	1.128	1.296	8.009	9.305	5.995	7.304	7.831



Table 7. 3

Calculated values of non-linearity parameter of aniline at 303.15 K

Pressure (MPa)	$\rho$ (gm cm <sup>-3</sup> )	$u$ (m sec <sup>-1</sup> )	$\chi'$	$J(c)$	$J(\chi')$	B/A	B/A	B/A	B/A
						Tong - Dong			
0.1	0.9871	1624.2	1.142	1.173	8.330	9.502	6.888	8.034	7.374
10	0.9917	1653.3	1.140	1.178	8.230	9.408	6.758	7.928	7.403
20	0.9962	1682.1	1.137	1.183	8.154	9.337	6.634	7.826	7.431
30	1.0005	1710.1	1.135	1.188	8.097	9.285	6.517	7.731	7.457
40	1.0047	1737.3	1.132	1.193	8.057	9.249	6.407	7.641	7.482
50	1.0088	1763.9	1.130	1.197	8.028	9.225	6.303	7.556	7.505
60	1.0127	1787.7	1.128	1.200	8.012	9.212	6.213	7.482	7.529
70	1.0166	1814.9	1.126	1.205	8.002	9.207	6.112	7.400	7.550
80	1.0203	1839.3	1.124	1.209	8.000	9.209	6.024	7.328	7.571
90	1.0240	1862.9	1.122	1.212	8.004	9.217	5.942	7.261	7.591
100	1.0275	1885.9	1.121	1.216	8.013	9.229	5.863	7.196	7.611
110	1.0310	1908.1	1.119	1.219	8.026	9.245	5.789	7.136	7.630
120	1.0343	1929.7	1.118	1.222	8.042	9.264	5.719	7.079	7.648
130	1.0376	1950.5	1.116	1.224	8.061	9.285	5.652	7.024	7.666
140	1.0409	1970.5	1.115	1.227	8.082	9.309	5.590	6.973	7.683
150	1.0440	1989.9	1.114	1.229	8.105	9.334	5.530	6.925	7.700
160	1.0471	2008.5	1.112	1.231	8.129	9.359	5.475	6.879	7.717

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## **Chapter-8**

Study of non-linearity parameter of binary liquid mixtures at elevated pressures

## Introduction:

Study of non-linearity parameter,  $B/A$ , of liquid mixtures<sup>(1-9)</sup> is important in view of the information it may yield on the interaction in liquid mixtures.  $B/A$  values of the liquids have been interpreted as the quantity representing the magnitude of the hardness of the liquid<sup>(10)</sup> which may be considered to be true for the liquid mixtures as well.

Sehgal and Porter<sup>(11)</sup> determined the  $B/A$  values for alcohol-water mixtures and Endo<sup>(12)</sup> calculated  $B/A$  for benzyl alcohol-ethanol system. Jugan<sup>(13)</sup> used the Tong -Dong method to calculate  $B/A$  for a number of binary liquid mixtures. Recently, Kuchhal et al<sup>(14)</sup> and Pandey et al<sup>(15,16)</sup> determined  $B/A$  values for pure liquids and binary liquid mixtures.

Although detailed studies of the non-linearity parameter of binary liquid mixtures have been reported, to the best of our knowledge, computation of  $B/A$  for liquid mixtures at elevated pressures has not been done so far.

In the present chapter, values of non-linearity parameter for binary liquid mixtures have been computed at elevated pressures applying four different methods<sup>(9,17-19)</sup>, and a comparative study is made. The thermodynamic parameters required to calculate  $B/A$  values of the liquid mixtures, are obtained from the Flory's statistical theory as discussed in chapter-2. Experimental values of sound velocity, density and other related properties of two binary mixtures (toluene + o-xylene & toluene + aniline) under taken for the present investigation, have been taken from the paper of Takagi et al<sup>(20)</sup>.

## Theory:

Equations (7.1), (7.2), (7.8) and (7.26) have been used to calculate the values of non-linearity parameter,  $B/A$ , of binary liquid mixtures under the present consideration at elevated pressures. The theoretical method employed has already been detailed out in chapter seven.

## Results and Discussion:

The two binary liquid mixtures under the present investigation are: toluene + o-xylene and toluene + aniline. The non-linearity parameter,  $B/A$ , of these liquid mixtures are calculated at elevated pressures ranging from 0.1 MPa to 160 MPa and at temperature of 303.15 K for four different mole fractions. Experimental values of ultrasonic velocity and density of the liquid mixtures are taken from the literature<sup>(20)</sup>.

For the parameters of liquid mixtures, needed for present calculation, we have used the Flory's theory in a manner as described in chapter-2.

The calculated values of  $B/A$  for toluene + o-xylene using different methods are reported in table 8.1. The values of  $x'$ ,  $J(o)$  and  $J(x')$  used in Tong-Dong method at different mole fractions for this system are reported in table 8.1(a). Similarly, table 8.2 enlists the values of  $B/A$  calculated through different methods for toluene + aniline system. Table 8.2(a) contains the values of  $x'$ ,  $J(o)$ ,  $J(x')$  for toluene + aniline.

A close perusal of tables-8.1 and 8.2 reveals that the  $B/A$  values calculated by Ballou's empirical relation and Hartmann's expression decrease as the pressure increases but the values of  $B/A$  computed by Sharma method show an opposite trend i. e. it increases as the pressure is increased.  $B/A$  values calculated by Tong-Dong method initially decrease with pressure upto a certain pressure, and after that it increase with the increase of pressure for both the mixtures. The value of pressure at which the trend changes decreases as the composition of toluene decreases in both the mixtures. Also, the non-linearity parameter decreases, in general, with the decrease in concentration of toluene in the mixtures upto a certain pressure. After this pressure, as the mole fraction of toluene in the mixtures decreases, the  $B/A$  values tend to increase.



Table 8.1(a)

Calculated values of  $x^*$ ,  $J(o)$ ,  $J(x^*)$  used in Tong-Dong method to calculate B/A of x-toluene + (1-x) o-xylene

Pressure (MPa)	$x = 0.8$				$x = 0.6$				$x = 0.4$				$x = 0.2$			
	$x^*$	$J(o)$	$J(x^*)$	B/A	$x^*$	$J(o)$	$J(x^*)$	B/A	$x^*$	$J(o)$	$J(x^*)$	B/A	$x^*$	$J(o)$	$J(x^*)$	B/A
0.1	1.149	1.177	8.621	9.798	1.145	1.182	8.440	9.622	1.142	1.186	8.315	9.501	1.139	1.190	8.212	9.402
10	1.144	1.192	8.369	9.561	1.141	1.196	8.253	9.449	1.138	1.200	8.169	9.369	1.135	1.204	8.103	9.307
20	1.140	1.205	8.216	9.421	1.138	1.206	8.137	9.343	1.134	1.206	8.080	9.286	1.132	1.207	8.040	9.247
30	1.136	1.214	8.125	9.339	1.133	1.217	8.066	9.283	1.131	1.216	8.032	9.249	1.128	1.217	8.010	9.227
40	1.130	1.225	8.059	9.284	1.130	1.227	8.024	9.251	1.128	1.228	8.006	9.233	1.125	1.228	8.000	9.228
50	1.130	1.234	8.023	9.257	1.127	1.235	8.005	9.241	1.125	1.236	8.000	9.236	1.122	1.237	8.006	9.242
60	1.127	1.243	8.005	9.247	1.125	1.244	8.000	9.244	1.122	1.245	8.007	9.252	1.120	1.244	8.022	9.266
70	1.125	1.249	8.000	9.249	1.123	1.249	8.004	9.254	1.120	1.251	8.021	9.272	1.118	1.252	8.046	9.298
80	1.123	1.257	8.005	9.262	1.120	1.257	8.019	9.276	1.118	1.258	8.042	9.300	1.116	1.259	8.074	9.333
90	1.121	1.263	8.016	9.279	1.118	1.264	8.038	9.302	1.116	1.264	8.069	9.333	1.114	1.264	8.104	9.368
100	1.119	1.268	8.031	9.299	1.117	1.269	8.060	9.329	1.115	1.269	8.093	9.362	1.113	1.268	8.130	9.397
110	1.117	1.274	8.054	9.328	1.115	1.275	8.090	9.366	1.113	1.274	8.125	9.399	1.111	1.274	8.171	9.445
120	1.115	1.280	8.081	9.361	1.113	1.280	8.120	9.401	1.111	1.281	8.165	9.446	1.109	1.280	8.213	9.493
130	1.114	1.284	8.108	9.392	1.112	1.285	8.153	9.438	1.110	1.285	8.200	9.486	1.108	1.284	8.252	9.536
140	1.113	1.288	8.133	9.421	1.110	1.289	8.181	9.470	1.108	1.290	8.238	9.528	1.107	1.288	8.286	9.574
150	1.111	1.292	8.162	9.454	1.109	1.293	8.214	9.507	1.107	1.292	8.268	9.561	1.105	1.292	8.327	9.619
160	1.110	1.296	8.195	9.491	1.108	1.297	8.251	9.547	1.106	1.296	8.305	9.602	1.104	1.296	8.370	9.666





Table 8.2(a)

Calculated values of  $x'$ ,  $J(x)$ ,  $J(x')$  used in Tong-Dong method to calculate B/A of x-toluene + (1-x) aniline

Pressure (MPa)	$x = 0.8$				$x = 0.6$				$x = 0.4$				$x = 0.2$			
	$x'$	$J(x)$	B/A	$J(x')$	$x'$	$J(x)$	B/A	$J(x')$	$x'$	$J(x)$	B/A	$J(x')$	$x'$	$J(x)$	B/A	$J(x')$
0.1	1.143	1.171	8.335	9.506	1.135	1.163	8.093	9.256	1.126	1.155	8.001	9.157	1.118	1.149	8.047	9.196
10	1.139	1.182	8.204	9.385	1.131	1.174	8.038	9.213	1.124	1.164	8.002	9.166	1.116	1.156	8.078	9.234
20	1.136	1.192	8.113	9.305	1.128	1.184	8.010	9.194	1.121	1.173	8.015	9.188	1.113	1.163	8.115	9.278
30	1.133	1.202	8.055	9.256	1.126	1.192	8.000	9.192	1.119	1.179	8.034	9.213	1.112	1.168	8.154	9.323
40	1.129	1.211	8.018	9.230	1.123	1.200	8.003	9.203	1.117	1.186	8.061	9.247	1.110	1.173	8.191	9.364
50	1.127	1.219	8.003	9.222	1.121	1.207	8.015	9.222	1.115	1.192	8.092	9.285	1.109	1.177	8.231	9.408
60	1.124	1.227	8.000	9.227	1.119	1.214	8.034	9.247	1.113	1.197	8.124	9.322	1.107	1.183	8.282	9.466
70	1.122	1.233	8.006	9.239	1.117	1.220	8.058	9.278	1.111	1.204	8.165	9.369	1.105	1.188	8.328	9.515
80	1.120	1.240	8.020	9.260	1.115	1.225	8.085	9.310	1.110	1.208	8.199	9.407	1.104	1.191	8.368	9.559
90	1.118	1.245	8.038	9.282	1.113	1.230	8.117	9.348	1.109	1.211	8.230	9.443	1.103	1.194	8.410	9.605
100	1.117	1.251	8.062	9.313	1.111	1.237	8.155	9.392	1.107	1.217	8.281	9.498	1.102	1.198	8.463	9.662
110	1.115	1.256	8.090	9.345	1.110	1.241	8.188	9.429	1.106	1.221	8.324	9.545	1.101	1.202	8.508	9.710
120	1.113	1.261	8.120	9.381	1.109	1.246	8.227	9.472	1.104	1.226	8.372	9.598	1.099	1.206	8.558	9.764
130	1.112	1.264	8.145	9.409	1.108	1.249	8.260	9.509	1.103	1.229	8.408	9.637	1.099	1.208	8.597	9.805
140	1.111	1.270	8.182	9.452	1.107	1.252	8.292	9.545	1.102	1.232	8.448	9.679	1.098	1.210	8.636	9.845
150	1.109	1.273	8.210	9.482	1.105	1.256	8.332	9.588	1.101	1.234	8.487	9.722	1.097	1.212	8.682	9.894
160	1.108	1.276	8.245	9.521	1.104	1.259	8.369	9.628	1.100	1.238	8.529	9.767	1.096	1.215	8.725	9.941

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